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Kleschick et al.

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[45] **Date of Patent: Dec. 12, 1989**

[54] **SUBSTITUTED 1,2,4-TRIAZOLO[1,5-A]PYRIMIDINE-2-SULFONYL CHLORIDES**

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Related U.S. Application Data

[60] Division of Ser. No. 940,480, Dec. 10, 1986, Pat. No. 4,818,273, which is a continuation-in-part of Ser. No. 768,353, Aug. 22, 1985, abandoned, which is a continuation-in-part of Ser. No. 551,758, Nov. 14, 1983, abandoned.

[51] **Int. Cl.**[4] **C07D 487/04**

[52] **U.S. Cl.** **544/263**; 564/336

[58] **Field of Search** 544/263, 256

[56] **References Cited**

U.S. PATENT DOCUMENTS

3,637,366	1/1972	Wietelmann et al. .	
3,920,690	11/1975	Harrington et al. .	
3,923,810	12/1975	Harrington et al. .	
4,036,840	7/1977	O'Brien	544/256
4,349,378	9/1982	Cliff et al. .	
4,444,774	7/1984	Dusza	544/256
4,605,433	8/1986	Pearson	71/90
4,638,075	1/1987	Kleschick et al.	544/263
4,727,017	2/1988	Pollet et al.	544/256
4,728,601	3/1988	Rauland et al.	544/256
4,772,720	9/1988	Kleschick et al.	548/262
4,830,663	5/1989	Dunbar	544/263

FOREIGN PATENT DOCUMENTS

0142811	5/1985	European Pat. Off.	544/263
27060	10/1973	Japan .	
951652	3/1964	United Kingdom	544/263
2149792	6/1985	United Kingdom	544/263

OTHER PUBLICATIONS

Broadbent et al., *J. Chem. Soc.*, 1965, pp. 3369–3372.

Okabe et al., *J. Fac. Agr.*, Kyushu University, 19, 91–102(1975).

Okabe et al., *J. Heterocyclic Chem.*, 20, 735(1983).

Novinson et al., *J. Med. Chem.*, 25, 420–426(1982).

Burgev, Medicinal Chemistry, 2d. Ed., Interscience (1960).

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[57] **ABSTRACT**

Novel substituted triazolo[1,5-a]pyrimidine-2-sulfonamides, e.g., 5,7-dimethyl-N-(2,6-dichlorophenyl)-1,2,4-triazolo[1,5-a]pyrimidine-2-sulfonamide and their agriculturally acceptable salt are prepared. These compounds and compositions containing them are useful for the control of unwanted vegetation. Novel substituted triazolo[1,5-a]pyrimidine-2-sulfonyl chlorides and substituted anilines and their use as intermediates are also described.

7 Claims, No Drawings

SUBSTITUTED 1,2,4-TRIAZOLO[1,5-A]PYRIMIDINE-2-SULFONYL CHLORIDES

CROSS-REFERENCE TO RELATED APPLICATION

This application is a divisional application of application Ser. No. 940,480, filed Dec. 10, 1986, now U.S. Pat. No. 4,818,273, which is a continuation-in-part of application Ser. No. 768,393, filed Aug. 22, 1985, now abandoned, which is a continuation in part of application Ser. No. 551,758, filed Nov. 14, 1983 now abandoned. The disclosure of the specification and claims of application Ser. No. 768,393 is hereby incorporated by reference.

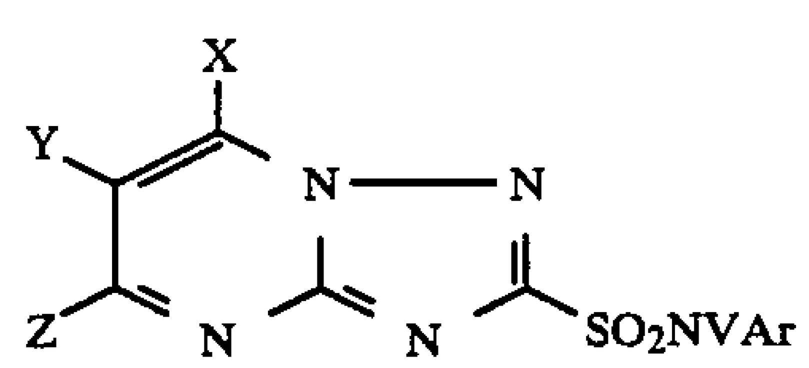
BACKGROUND OF THE INVENTION

In recent years there has been a great deal of effort directed to the development of sulfonamides having herbicidal activity and several of these compounds have reached the stage of commercialization, i.e., chlorosulfuron and sulfometuron methyl. These compounds exhibit both preemergence and postemergence activity against undesirable vegetation and, in addition, have a low toxicity to mammals. The compounds of the prior art may be depicted as follows:

wherein Ar is usually a benzene derivative and Ar' is usually a pyrimidine or symmetrical triazine derivative.

In addition, there are a number of other sulfonamide herbicides that have been commercialized, for example, methyl sulfanilylcarbamate; O,O-diisopropyl phosphorodithioate-S-ester with N-(2-mercaptoethyl)benzenesulfonamide; 3-isopropyl-1H-2,1,3-benzothiadiazin-4(3H)-one-2,2-dioxide; N-[2,4-dimethyl-5-[[(trifluoromethyl)sulfonyl]amino]phenyl]acetamide and 3,5-dinitro-N^4, N^4-dipropylsulfanilamide.

It has now been found that novel compounds having the formula:



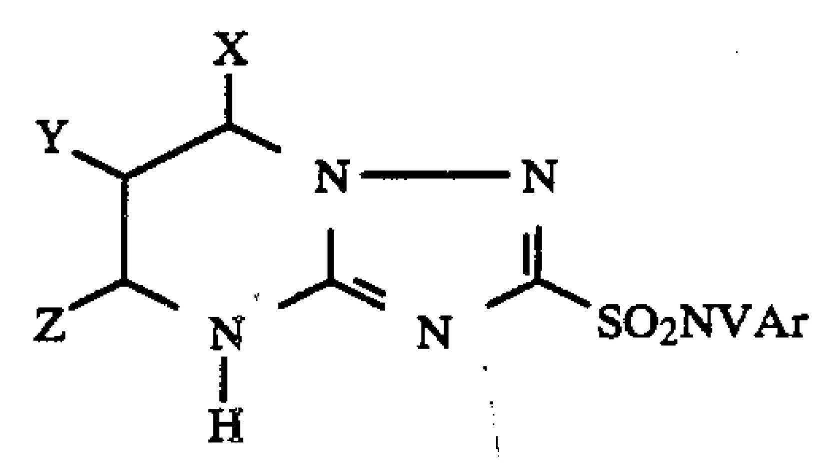
I

wherein

Ar represets an aromatic or heteroaromatic ring chosen from among phenyl; 1- or 2-naphthyl; 2-, 3- or 4-pyridyl; 2-or 3-thienyl; 2- or 3-furyl; 2-, 4-, or 5-thiazolyl; 2-, 4-, or 5-imidazolyl; 2-, 4-, or 5-oxazolyl; 3-, 4-, or 5-isothiazolyl; 3-, 4-, or 5-isoxazolyl; 3-, 4-, or 5-pyrazolyl; 2-benzthiazolyl; 2-benzoxazolyl; 2-benzimidazolyl: or 1-benztriazolyl; and Ar is unsubstituted except in the case of where Ar is phenyl or Ar is substituted with one to five substituents chosen from among C_1–C_6 alkyl; benzyl; halo; C_1–C_6 mono- or polyhaloalkyl; phenyl; phenyl substituted with one or more groups chosen from halo, C_1–C_6 alkyl, or C_1–C_6 haloalkyl; hydroxy; C_1–C_6 alkoxy; C_1–C_6 mono- or polyhaloalkoxy; phenoxy; phenoxy substituted with one or more groups chosen from halo, C_1–C_6 alkyl or C_1–C_6 haloalkyl; 2-pyridyloxy; 2-pyridyloxy substituted with one or more groups, chosen from halo, C_1–C_6 alkyl or C_1–C_6 haloalkyl; amino; C_1–C_6 alkylamino; C_1–C_6 dialkylamino; nitro; C_1–C_6 alkylthio; C_1–C_6 polyhaloalkylthio; C_1–C_6 alkylsulfinyl; C_1–C_6 polyhaloalkylsulfinyl; C_1–C_6 alkylsulfonyl; C_1–C_6 polyhaloalkylsulfonyl; phenylthio; phenylthio substituted with one or more groups chosen from halo, C_1–C_6 alkyl or C_1–C_6 haloalkyl; phenylsulfinyl; phenylsulfinyl substituted with one or more groups chosen from halo, C_1–C_6 alkyl, or C_1–C_6 haloalkyl; phenylsulfonyl; phenylsulfonyl substituted with one or more groups chosen from halo, C_1–C_6 alkyl, or C_1–C_6 haloalkyl; cyano; carboxyl; C_1–C_{10} alkoxycarbonyl; phenoxycarbonyl; phenoxycarbonyl substituted withone or more groups chosen from halo, C_1–C_6 alkyl or C_1–C_6 haloalkyl; alkoxyalkoxycarbonyl wherein the number of carbons in the alkoxyalkoxy fragment ranges from 2–10 and the number of oxygens in the alkoxyalkoxy fragment ranges from 2–4; 2-pyridylmethoxycarbonyl; dialkylaminoalkoxycarbonyl wherein the number of carbons in the dialkylaminoalkoxy fragment ranges from 3–10 and the number of oxygens in the dialkylaminoalkoxy fragment is one; C_3–C_6 alkenyloxycarbonyl; $COON{=}C(R^{14})(R^{14})$ wherein each R^{14} independently represents hydrogen, C_1–C_6 alkyl or phenyl; amino-, C_1–C_6 alkylamino-, or di C_1–C_6 alkylaminocarbonyl; C_1–C_{10} alkoxysulfonyl; C_1–C_4 polyhaloalkoxysulfonyl; di C_1–C_6 alkylaminosulfonyl; formyl; C_1–C_6 alkylcarbonyl; C_1–C_6 mono- or polyhaloalkylcarbonyl; phenylcarbonyl; phenylcarbonyl substituted with one or more groups chosen from halo, C_1–C_6 alkyl or C_1–C_6 haloalkyl; or $C(R^{15})(R^{15})OR^{16}$ wherein each R^{15} independently represents hydrogen or C_1–C_6 alkyl and R^{16} represents hydrogen, C_1–C_6 alkyl, benzyl, phenylcarbonyl or C_1–C_6 alkylcarbonyl (except in the cases of thio, sulfinyl, and sulfonyl substituents where if one of these substituents is present the other one to four Ar substituents may not be chosen from among the other two; oxycarbonyl substituents where the other one to four Ar substituents may not be chosen from among different oxycarbonyl substituents; or aminocarbonyl substituents where the other one to four Ar substituents may not be chosen from among different aminocarbonyl substituents); X, Y, and Z independently represent hydroxyl; carboxyl; hydrogen; C_1–C_6 alkyl; C_1–C_6 mono- or polyhaloalkyl; C_1–C_6 alkoxy; C_1–C_6 mono- or polyhaloalkoxy; amino, C_1–C_4 alkylamino, or di C_1–C_4 alkylamino; phenyl; phenyl substituted with one or more groups chosen from halo, nitro, C_1–C_6 alkyl, or C_1–C_6 mono- or polyhaloalkyl; C_1–C_6 alkylthio; halo; or two adjacent substituents (i.e., X and Y or Y and Z) are joined together to form a five, six, or seven-membered saturated cyclic structure of carbon atoms or one said carbon atom of X,Y or Y,Z is replaced by a heteroatom chosen from among nitrogen, oxygen, or sulfur (i.e., X,Y or Y,Z is $-(CH_2)_n-$ wherein n is 3, 4, or 5; or X,Y or Y,Z is $-(CH_2)_n-A-(CH_2)_m-$ wherein n is 0–4, the value of m is equal to the ring size minus $(n+3)$ and A is NH, O, or S); and V is H or R and R represents C_1–C_{10} alkyl, C_3–C_{10} alkenyl, C_3–C_{10} alkynyl, phenylalkyl, C_2–C_{10} alkanoyl, C_1–C_{10} alkoxycarbonyl, phenoxycarbonyl, di C_1–C_6 alkylaminocarbonyl, C_1–C_6 alkylsulfonyl, phenylsulfonyl, C_1–C_{10} alkoxythiocarbonyl or phenoxythiocarbonyl, wherein alkyl, alkenyl, alkynyl, and alkoxy in each instance is optionally substituted by halo and each phenyl moiety is optionally substituted by one or two groups selected from halo, nitro, C_1–C_4 alkyl, or C_1–C_4 haloalkyl; and, when V represents hydrogen, agriculturally acceptable salts thereof are useful pre- and post-emergence herbicides or intermediates for preparing herbicides.

Treatment of the locus of undesired vegetation or weeds with the novel compounds or with compositions containing herbicidally effective amounts of the novel compounds in admixture with one or more inert carriers can be used to obtain broad spectrum or selective weed control depending upon the specific compound and the amount applied. Broadleaf weeds are particularly susceptible to the compounds and control of undesirable vegetation in crops such as wheat, rice, corn, soybeans, and cotton can be achieved. Aquatic vegetation is controlled by the compounds.

In addition, certain novel tetrahydro derivatives of the compounds of general Formula I, which can be represented by Formula II



II

wherein X, Y, A, V, and Ar as defined hereinabove and their agriculturally acceptable salts also exhibit herbicidal activity.

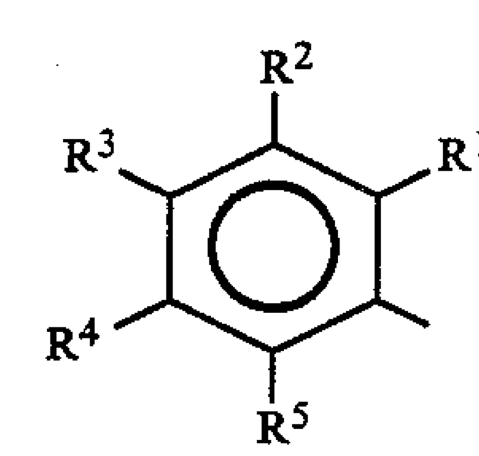
The invention further encompasses certain of the novel substituted triazolo[1,5-a]pyrimidine-2-sulfonyl chlorides and certain of the novel substituted anilines which are useful in preparing the compounds of Formulae I and II.

DETAILED DESCRIPTION OF THE INVENTION

The contemplated aromatic or heteroaromatic ring systems, Ar, of Formula I include substituted or unsubstituted (except for phenyl, which must be substituted) phenyl; 1- or 2-naphthyl; 2-, 3- or 4-pyridyl; 2- or 3-thienyl; 2-or 3-furyl; 2-, 4- or 5-thiazolyl; 2-, 4- or 5-imidazolyl; 2-, 4- or 5-oxazolyl; 3-, 4- or 5-isothiazolyl; 3-, 4- or 5-isoxazolyl; 3-, 4- or 5-pyrazolyl; 2-benzthiazolyl; 2-benzoxazolyl; 2-benzimidazolyl and 1-benztriazolyl. Typical examples of substituents found on the aromatic or heteroaromatic ring systems may be one, more than one, or a combination of the following: halo, C_1–C_6 alkyl, benzyl, C_1–C_6 mono- or polyhaloalkyl, phenyl (optionally substituted with one or more groups chosen from halo, C_1–C_6 alkyl, or C_1–C_6 haloalkyl), hydroxy, C_1–C_6 alkoxy, C_1–C_6 mono- or polyhaloalkoxy, phenoxy or yridyloxy (each optionally substituted with one or more groups chosen from halo, C_1–C_6 alkyl or C_1–C_6 haloalkyl), nitro, amino, C_1–C_6 alkylamino, di C_1–C_6 alkylamino, C_1–C_6 alkylthio, C_1–C_6 polyhaloalkylthio, C_1–C_6 alkylsulfinyl, C_1–C_6 polyhaloalkylsulfinyl, C_1–C_6 alkylsulfonyl, C_1–C_6 polyhaloalkylsulfonyl, phenylthio or phenylsulfinyl or phenylsulfonyl (each phenyl optionally substituted wit one or more groups chosen from halo, C_1–C_6 alkyl, or C_1–C_6 haloalkyl), cyano, carboxylic acids and derivatives of carboxylic acids (esters derived from available alcohols and amides derived from ammonia or available primary and secondary amines, which can be termed oxycarbonyl and aminocarbonyl substituents) including C_1–C_{10} alkoxycarbonyl, pheoxycarbonyl optionally substituted with one or more groups chosen from halo, C_1–C_6 alkyl, or C_1–C_6 haloalkyl, alkoxyalkoxycarbonyl wherein the number of carbons in the alkoxyalkoxy fragment ranges from 2–10 and the number of oxygens in the alkoxyalkoxy fragment ranges from 2–4, 2-pyridylmethoxycarbonyl, dialkylaminoalkoxycarbonyl wherein the number of carbons in the dialkylaminoalkoxy fragment ranges from 3–10 and the number of oxygens in the dialkylaminoalkoxy fragment is one, C_3–C_6 alkenyloxycarbonyl, $COON{=}C(R^{14})(R^{14})$ wherein each R^{14} independently represents hydrogen, C_1–C_6 alkyl, or phenyl, C_1–C_{10} alkoxysulfonyl, C_1–C_4 polyhaloalkoxysulfonyl, amino- or C_1–C_6 alkylamino or di C_1–C_6 alkylaminocarbonyl, di C_1–C_6 alkylaminosulfonyl, formyl, C_1–C_6 alkylcarbonyl; C_1–C_6 mono- or polyhaloalkylcarbonyl, phenylcarbonyl (optionally substituted with one or more groups selected from halo, C_1–C_6 alkyl, or C_1–C_6 haloalkyl), or $C(R^{15})(R^{15})OR^{16}$ wherein each R^{15} independently represents hydrogen or C_1–C_6 alkyl and R^{16} represents hydrogen, C_1–C_6 alkyl, benzyl, phenylcarbonyl, or C_1–C_6 alkylcarbonyl. In cases where one substituent is a thio, sulfinyl, or sulfonyl moiety, other substituents may not be chosen from among the other two. Also, in cases where one substituent is an oxycarbonyl moiety, other substituents may not be chosen from among other oxycarbonyl moieties; and where one substituent is an aminocarbonyl moiety, other substituents may not be chosen from among other aminocarbonyl moieties. Halo in each instance represents fluoro, chloro, bromo, or iodo.

Compounds of Formula I wherein Ar represents substituted phenyl or substituted or unsubstituted 1- or 2-naphthyl; 2-, 3-, or 4-pyridyl; 2- or 3-thienyl; or 3-, 4-, or 5-pyrazolyl are preferred. Those wherein Ar represents substituted phenyl, substituted 1-naphthyl, or substituted 3-, 4-, or 5-pyrazolyl are more preferred.

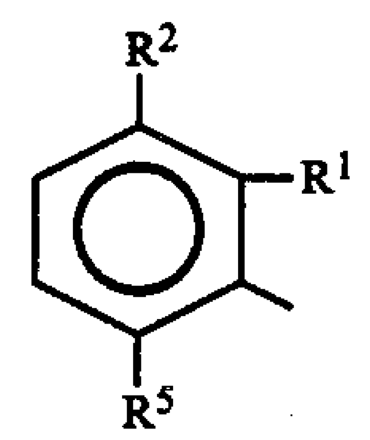
In the case of the more preferred compounds of Formula I wherein Ar is substituted phenyl, Ar can be depicted as the formula



wherein R^1, R^2, R^3, R^4, and R^5 independently represent each of the Ar substituents (with each of the listed exceptions) noted in the Summary of the Invention and in the foregoing discussion, or hydrogen, provided not all are hydrogen. Of those substituents, the following are preferred. R^1 represents F, Cl, Br, I, $—NO_2$, phenyl, phenoxy (optionallysubstituted by one or more substituents selected from F, Cl, Br, I, C_1–C_4 alkyl, and C_1–C_4 haloalkyl), $—CF_3$, $—OCF_3$, OCF_2CF_2H, $—OCF_2CCl_2H$, $—OCH_2CF_3$, $—SCF_3$, $—SCF_2CF_2H$, $—SCF_2CCl_2H$, $—SOCF_3$, $—SOCF_2CF_2H$, $—SOCF_2CCl_2H$, $—SO_2CF_3$, $—SO_2CF_2CF_2H$, $—SO_2CF_2CCl_2H$, $—SR^6$, $—SOR^6$, $—SO_2R^6$, —CN, $—COOR^7$, $—CONH_2$, $—CONHR^8$, $—CONR^8R^8$, $—SO_3R^8$, or $SO_3CH_2CF_3$; R^2 and R^4 represent H, F, Cl, Br, I, C_1–C_4 alkyl, $—COOR^7$, or $—OR^8$; R^3 is H; and R^5 represents H, phenyl, C_1–C_4 alkyl, C_1–C_4 alkoxy, F, Cl, Br, I, $—NO_2$, $—CF_3$, $—OCF_3$, $—OCF_2CF_2H$, $—OCF_2CCl_2H$, $—OCH_2CF_3$, $—SCF_3$, $—SCF_2CF_2H$, $—SCF_2CCl_2H$, $—SOCF_3$, $—SOCF_2$ CF_2H, $—SOCF_2CCl_2H$, $—SO_2CF_3$, $—SO_2CF_2CF_2H$,

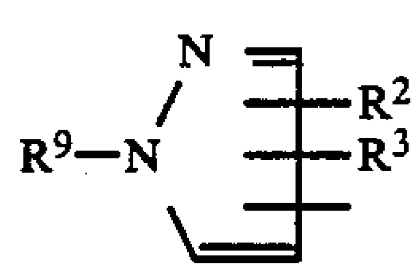
—$SO_2CF_2CCl_2H$, —SR^6, —SOR^6, —SO_2R^6, —CN, —$COOR^7$, —$CONH_2$, —$CONHR^8$, —$CONR^8R^8$, —SO_3R^8, —$SO_3CH_2CF_3$, or —$CR^6R^6OR^6$, wherein R^6 represents H or C_1–C_4 alkyl, R^7 represents C_1–C_6 alkyl, C_3**14** C_4 alkenyl, C_3–C_4 alkynyl, C_1–C_4 alkoxy C_2–C_3 alkyl, phenyl (optionally substituted by one or two substituents selected from F, Cl, Br, I, C_1–C_4 alkyl, and C_1–C_4 haloalkyl), or 2-pyridylmethyl and R^8 represents C_1–C_4 alkyl.

Compounds of Formula I in which Ar is represented by the formula



wherein R^1 represents C_1–C_4 alkyll, F, Cl, Br I, —NO_2, —SR^6, —SOR^6, —SO_2R^6, —$COOR^7$, or —CF_3; R^2 represents H, F, Cl, Br, I, C_1–C_4 alkyl, or —$COOR^7$ and R^5 represents H, C_1–C_4 alkyl, C_1–C_4 alkoxy, F, Cl, Br, I, —CH_2OR^6, phenyl, —NO_2, or —$COOR^7$ wherein R^6 represents C_1–C_4 alkyl and R^7 represents C_1–C_4 alkyl, C_3–C_4 alkenyl, C_3–C_4 alkynyl, 2-ethoxyethyl or 2-pyridylmethyl are most especially preferred.

In the case of the more preferred compounds of Formula I wherein Ar represents 3-, 4-, or 5-pyrazolyl, Ar can be depicted as the formula



wherein R^2 and R^3 independently represent each of the substituents (with each of the listed exceptions) noted in the Summary of the Invention and in the foregoing discussions and R^9 represents hydrogen or C_1–C_6 alkyl. Preferred compounds of this type include those wherein R^2 and R^3 each independently represents H, C_1–C_4 alkyl, benzyl, F, Cl, Br, I, NO_2, CF_3, OCF_3, C_1–C_4 alkoxy, C_1–C_{10} alkoxycarbonyl, C_3–C_6 alkenyloxycarbonyl, benzyloxycarbonyl, or amino-, C_1–C_4 alkylamino- or di C_1–C_4 alkylaminocarbonyl.

The substituents on the triazolopyrimidine fragment of Formula I are represented by X, Y, and Z. Substituents X, Y, and Z independently represent hydroxyl, carboxyl, hydrogen, C_1–C_6 alkyl, C_1–C_6 mono- or polyhaloalkyl, C_1–C_6 alkoxy, C_1–C_6 mono- or polyhaloalkoxy, amino, C_1–C_4 alkylamino, di C_1–C_4 alkylamino, phenyl (optionally substituted wit one or more groups chosen from F, Cl, Br, I, nitro, C_1–C_6 alkyl, or C_1–C_6 mono- or polyhaloalkyl), C_1–C_6 alkylthio, halogen, or two adjacent substituents (i.e. X and Y or Y and Z) are joined together to form a saturated five, six, or seven-membered saturated cyclic structure of carbon atoms or up to one heteroatom chosen from among nitrogen, oxygen, or sulfur (i.e. X,Y or Y,Z is —$(CH_2)_n$— wherein n is 3, 4, or 5; or X,Y or Y,Z is —$(CH_2)_n$—A—$(CH_2)_m$— wherein n is 0–4, the value of m is equal to the ring size minus (n+3) and A is NH, O, or S).

Compounds of Formula I wherein X, Y, and Z independently represent H, F, Cl, Br, I, C_1–C_4 alkyl, C_1–C_4 alkoxy, C_1–C_4 alkylthio, C_1–C_4 haloalkyl are preferred.

The most highly preferred compounds of the invention are those compounds of Formula I wherein X represent H, CH_3, CF_3, OCH_3, OC_2H_5, or SCH_3; or Y represents H, Cl, or CH_3; or Z represents H, CH_3, or OCH_3; and Ar represents substituted phenyl wherein R^1 represents F, Cl, Br, CF_3, NO_2, or C_1–C_4 alkoxycarbonyl; or R^2 represents H or CH_3; or R^5 represents H, F, Cl, Br, OCH_3, or CH_3; and R^3 and R^4 represent hydrogen and their agriculturally acceptable salts. Additional most highly preferred compounds are those compounds of Formula I wherein X or Y or Z are as defined above and Ar represents 3-, 4-, or 5-pyrazolyl wherein R^9 represents H, CH_3, or C_2H_5; or R^2 and R^3 independently represent H, CH_3, CF_3, or C_1–C_4 alkoxycarbonyl and their agriculturally acceptable salts.

The substituent V of Formulae I and II represents any of the following: hydrogen, alkyl, alkenyl, alkynyl, phenylalkyl, substituted phenylalkyl, alkanoyl, alkoxycarbonyl, phenoxycarbonyl, dialkylaminocarbonyl, alkylsulfonyl, phenylsulfonyl, alkylthiocarbonyl, or phenylthiocarbonyl wherein alkyl, alkenyl, and alkynyl are as defined above and each phenyl group is optionally substituted as defined above.

Preferred derivatives of the invention are those compounds of Formula I wherein V represents hydrogen, C_1–C_4 alkyl, allyl, benzyl, —COR^{13}, —CO_2R^{13}, —$CONR^{13}R^{13}$, —$CSOR^{13}$, and —SO_2R^{13}, wherein R^{13} is C_1–C_6 alkyl, phenyl (optionally substituted by one or more groups chosen from halo, C_1–C_6 alkyl, or C_1–C_6 haloalkyl), or C_1–C_2 haloalkyl.

The more preferred derivatives of the invention with respect to V are those wherein V represents hydrogen, C_1–C_4 alkyl, allyl, benzyl, C_2–C_4 alkanoyl, C_2–C_3 haloalkanoyl, benzoyl, C_1–C_4 alkoxycarbonyl, phenoxycarbonyl, di C_1–C_4 alkylaminocarbonyl, C_1–C_4 alkoxythiocarbonyl, C_1–C_4 alkylsulfonyl, C_1–C_2 haloalkylsulfonyl, or phenylsulfonyl, each phenyl optionally substituted by one or more groups chosen from among halo, nitro, methyl, and trifluoromethyl. The most preferred compounds in this regard are those wherein V represents hydrogen, C_2–C_4 alkanoyl, C_1–C_4 alkoxycarbonyl, or di C_1–C_4 alkylaminocarbonyl.

Substituted 1,2,4-triazolo[1,5-a]pyrimidine-2-sulfonamides and their tetrahydro derivatives behave as acids due to the presence of a sulfonamide moiety proton and consequently form salts when treated with bases. The term "agriculturally acceptable salts" is employed in this application to denote compounds wherein the acidic sulfonamide proton of the compounds of Formulae I and II and replaced by a cation which is not herbicidal, especially to crop plants, nor significantly deleterious to the applicator, the environment, or the ultimate user of any crop being treated. Suitable cations include, for example, those derived from alkali or alkaline earth metals and those derived from ammonia and amines. Preferred cations include sodium, potassium, magnesium, and aminium cations of the formula

$$R^{10}R^{11}R^{12}NH^{\oplus}$$

wherein R^{10}, R^{11}, and R^{12} each, independently represents hydrogen or C_1–C_{12} alkyl, C_3–C_{12} cycloalkyl, or C_3–C_{12} alkenyl, each of which is optionally substituted by one or more hydroxy, C_1–C_8 alkoxy, C_1–C_8 alkylthio or phenyl groups. Additionally, any two of R^{10}, R^{11}, and R^{12} together represent an aliphatic difunctional moiety containing 1 to 12 carbon atoms and up to two oxygen or sulfur atoms. Sodium, potassium, ammonium, and triethanolaminium are most preferred cations.

Specifically preferred compounds include the compounds of Formula I given in the following examples and, except for examples 38 and 39, their agriculturally acceptable salts.

1. 5,7-Dimethyl-N-(2,6-dichlorophenyl)-1,2,4-triazolo[1,5-a]pyrimidine-2-sulfonamide
2. 5-Methyl-N-(2,6-dichlorophenyl)-1,2,4-triazolo[1,5-a]pyrimidine-2-sulfonamide
3. 5-Methyl-N-(2-bromo-6-chlorophenyl)-1,2,4-triazolo[1,5-a]pyrimidine-2-sulfonamide
4. 5-Methyl-N-(2,6-difluoro-3-methylphenyl)-1,2,4-triazolo[1,5-a]pyrimidine-2-sulfonamide
5. 5-Methyl-N-(2,6-difluorophenyl)-1,2,4-triazolo[1,5-a]pyrimidine-2-sulfonamide
6. 5,7-Dimethoxy-N-(2,6-dichloro-3-methylphenyl)-1,2,4-triazolo[1,5-a]pyrimidine-2-sulfonamide
7. 5,7-Dimethoxy-N-(2-methoxy-6-trifluoromethylphenyl)-1,2,4-triazolo[1,5-a]pyrimidine-2-sulfonamide
8. 5-Methyl-7-methylthio-N-(2,6-dichlorophenyl)-1,2,4-triazolo[1,5-a]pyrimidine-2-sulfonamide
9. 5-Methyl-7-methylthio-N-(2-trifluoromethylphenyl)-1,2,4-triazolo[1,5-a]pyrimidine-2-sulfonamide
10. 7-Ethoxy-5-methyl-N-(2,6-dichloro-3-methylphenyl)-1,2,4-triazolo[1,5-a]pyrimidine-2-sulfonamide
11. 5,7-Dimethyl-N-(2-chloro-6-phenylphenyl)-1,2,4-triazolo[1,5-a]pyrimidine-2-sulfonamide
12. 5-Methyl-N-(2-methyl-6-nitrophenyl)-1,2,4-triazolo[1,5-a]pyrimidine-2-sulfonamide
13. 5-Methyl-N-(2-chloro-6-methylphenyl)-1,2,4-triazolo[1,5-a]pyrimidine-2-sulfonamide
14. 6-Methyl-N-(2-bromo-6-methylphenyl)-1,2,4-triazolo[1,5-a]pyrimidine-2-sulfonamide
15. 6-Methyl-N-(2-fluoro-6-chlorophenyl)-1,2,4-triazolo[1,5-a]pyrimidine-2-sulfonamide
16. 6-Methyl-N-(2-chloro-6-methylphenyl)-1,2,4-triazolo[1,5-a]pyrimidine-2-sulfonamide
17. 6-Methyl-N-(2-methyl-6-nitrophenyl)-1,2,4-triazolo[1,5-a]pyrimidine-2-sulfonamide
18. 7-Ethoxy-5-methyl-N-(2-trifluoromethylphenyl)-1,2,4-triazolo[1,5-a]pyrimidine-2-sulfonamide
19. 7-Methoxy-5-methyl-N-(2,6-dichloro-3-methylphenyl)-1,2,4-triazolo[1,5-a]pyrimidine-2-sulfonamide
20. 7-Ethoxy-5-methyl-N-(2-bromo-6-chloro-3-methylphenyl)-1,2,4-triazolo[1,5-a]pyrimidine-2-sulfonamide
21. 5,7-Dimethoxy-N-(2,6-dibromo-3-methylphenyl)-1,2,4-triazolo[1,5-a]pyrimidine-2-sulfonamide
22. Methyl 3-methyl-N-(5,7-dimethyl-1,2,4-triazolo[1,5-a]pyrimidine-2-sulfonyl)anthranilate.
23. Methyl 3-methyl-N-(7-ethoxy-5-methyl-1,2,4-triazolo[1,5-a]pyrimidine-2-sulfonyl)anthranilate.
24. Methyl 3-fluoro-N-(6-chloro-1,2,4-triazolo[1,5-a]-pyrimidine-2-sulfonyl)anthranilate.
25. 5,7-Dimethoxy-N-(2,6-dichlorophenyl)-1,2,4-triazolo[1,5-a]pyrimidine-2-sulfonamide.
26. 7-Methyl-N-(2,6-dichlorophenyl)-1,2,4-triazolo[1,5-a]pyrimidine-2-sulfonamide.
27. N-(2,6-dichlorophenyl)-1,2,4-triazolo[1,5-a]pyrimidine-2-sulfonamide.
28. 7-Ethoxy-5-methyl-N-(2,6-dibromo-3-methylphenyl)-1,2,4-triazolo[1,5-a]pyrimidine-2-sulfonamide.
29. 6-Chloro-N-(2,6-difluorophenyl)-1,2,4-triazolo[1,5-a]pyrimidine-2-sulfonamide.
30. 5-Methyl-7-trifluoromethyl-N-(2-methoxy-6-trifluoromethylphenyl)-1,2,4-triazolo[1,5-a]pyrimidine-2-sulfonamide.
31. 5,7-Dimethyl-N-(1,3-dimethyl-5-trifluoromethyl-4-pyrazolyl)-1,2,4-triazolo[1,5-a]pyrimidine-2-sulfonamide.
32. 5-Methyl-N-(1,3-dimethyl-5-trifluoromethyl-4-pyrazolyl)-1,2,4-triazolo[1,5-a]pyrimidine-2-sulfonamide.
33. 5,7-Dimethyl-N-(1-methyl-4-ethoxycarbonyl-4-pyrazolyl)-1,2,4-triazolo[1,5-a]pyrimidine-2-sulfonamide.
34. 5,7-Dimethoxy-N-(2-chloro-1-naphthyl)-1,2,4-triazolo-[1,5-a]pyrimidine-2-sulfonamide.
35. 5-Methyl-N-(2-chloro-1-naphthyl)-1,2,4-triazolo-[1,5-a]pyrimidine-2-sulfonamide.
36. 5-Methyl-7-methoxy-N-(2-chloro-1-naphthyl)-1,2,4-triazolo[1,5-a]pyrimidine-2-sulfonamide.
37. 5-Methyl-7-ethoxy-N-(2-chloro-1-naphthyl)-1,2,4-triazolo[1,5-a]pyrimidine-2-sulfonamide.
38. 5-Methyl-N-(2-methylpropanoyl)-N-(2,6-difluorophenyl)-1,2,4-triazolo[1,5-a]pyrimidine-2-sulfonamide.
39. 5-Methyl-N-acetyl-N-(2,5-dichlorophenyl)-1,2,4-triazolo[1,5-a]pyrimidine-2-sulfonamide.

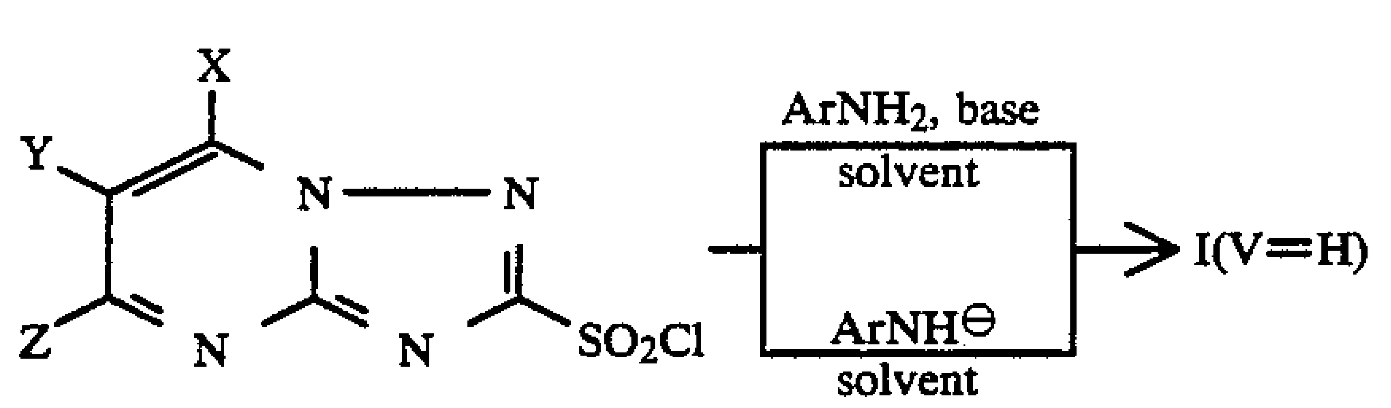
Specially preferred compounds of Formula II include the following and their agriculturally acceptable salts:

1. 5,7-Dimethyl-N-(2,6-dichlorophenyl)-4,5,6,7-tetrahydro-1,2,4-triazolo[1,5-a]pyrimidine-2-sulfonamide
2. 5-Methyl-N-(2,6-dichlorophenyl)-4,5,6,7-tetrahydro-1,2,4-triazolo[1,5-a]pyrimidine-2-sulfonamide
3. 5,7-Dimethyl-N-(2-trifluoromethylphenyl)-4,5,6,7-tetrahydro-1,2,4-triazolo[1,5-a]pyrimidine-2-sulfonamide

Furthermore, in the compounds corresponding to general Formula II, the existence of stereoisomerism is possible. For example, stereoisomeric relationships exist when at least one of substituents X, Y, and Z does not equal hydrogen. When only one of substituents X, Y, and Z does not equal hydrogen, the compound of Formula II may exist as a mixture of enantiomers. One enantiomer will be designated as having the R-configuration and the other will be designated as having the S-configuration. Each enantiomer may exhibit different levels of herbicidal activity. When two or more of substituents X, Y, or Z in Formula II do not equal hydrogen, the material may exist as a mixture of diastereomers. For example, when two substituents among X, Y and Z do not equal hydrogen, the compound may exist as two diastereomers. When all three of substituents X, Y and Z do not equal hydrogen the compound may exist as four diastereomers. In addition all of the diastereomers described above exist as a mixture of two enantiomers. All of the stereoisomers described above, diastereomers and their enantiomeric pairs, may exhibit different levels of herbicidal activity.

The synthesis of compounds of general Formula I can be carried out in a straightforward manner as illustrated in Scheme I. Reaction of a sulfonyl chloride of Formula IV with the appropriate aromatic (substituted or unsubstituted) or heteroaromatic (substituted or unsubstituted) amino compound ($ArNH_2$) under basic conditions yields the desired product of Formula I. A wide range of solvents may be employed (i.e., CH_2Cl_2, CH_3CN or pyridine) at temperatures ranging from 0° C. to reflux. Bases which serve as catalysts include pyridine, 4-dimethylaminopyridine and tertiary alkylamines such as triethylamine or N-methylmorpholine. Generally the amino compound serves as the limiting reagent. Molar ratios of between 1.1 and 1.0 for the sulfonyl chloride to amino compound and molar ratios of between 5.0 and 1.1 for the base to amino compound are used most often. A wide range of concentrations may be employed (i.e., 0.1–5M). Generally concentrations in the range of 0.5–2M are used to give a homogeneous reaction which proceeds at a convenient rate. In addition it is sometimes advantageous to use a combination of pyridine derived base catalysts and tertiary amine bases. The use of pyridine as a solvent is convenient as the pyridine can serve both as the solvent and the catalyst in the transformation.

SCHEME I



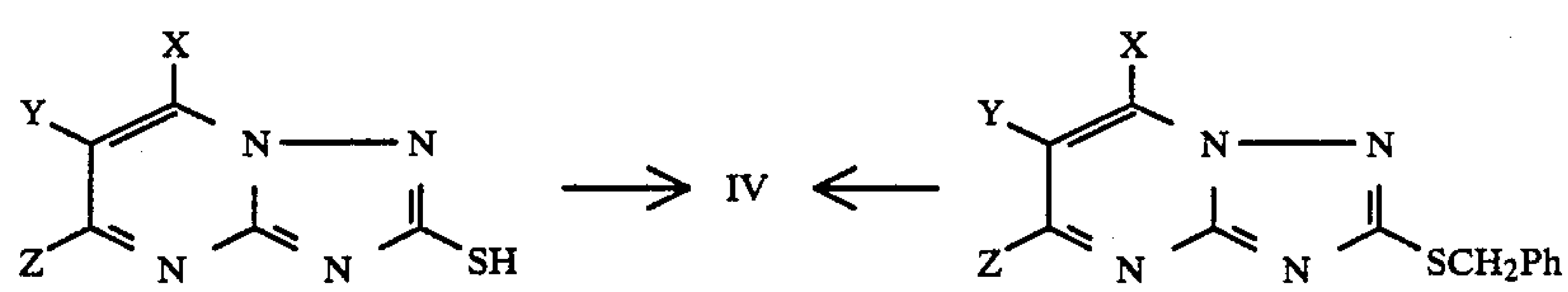
IV

An alternative route to compounds of Formula I is also illustrated in Scheme I. In cases where the amino compound ($ArNH_2$) is less reactive (less nucleophilic) is it advantageous to prepare a metal derivative of the amino compound by treatment with a strong base. The metal derivatives are generally prepared in ether solvents (i.e., THF) using strong bases such as alkali metal alkyls (i.e., n-BuLi) or alkali metal hydrides (i.e., NaH or KH) at temperatures ranging from −80° C. to 0° C. The amide anion thus generated in situ can be reacted with a sulfonyl chloride of Formula IV to yield the desired product of Formula I. Generally, molar ratios of the starting amino compound to sulfonyl chloride of 2 to 3 are used to ensure complete reaction

The method of U.S. application Ser. No. 795,818, filed on Nov. 11, 1985, which method employs the condensation of N-trialkylsilylanilines with sulfonyl chlorides of Formula IV to produce compounds of Formula I, can also be used and is especially valuable in laboratory operations.

Sulfonyl chlorides of Formula IV represent key intermediates in the synthesis of sulfonamides of Formula I. Sulfonyl chlorides of Formula IV may be prepared according to routes outlined in Scheme II. Mercaptans of Formula V may be converted to sulfonyl chlorides of Formula IV by treatment with chlorine in an aqueous acidic medium. Generally the medium would be aqueous acetic acid or aqueous HCl. The temperature of the reaction mixture is generally maintained between −20° C. and 25° C. during the course of the chlorine addition. Most preferably, temperature ranges between −20° C. and 0° C. are employed to minimize unwanted side reactions such as hydrolysis of the compound of Formula IV to the corresponding sulfonic acid. Alternatively, the mercaptan of Formula V may be suspended in a two phase system of aqueous acid (i.e., HCl) and an organic solvent (i.e., CH_2Cl_2) and treated with sodium hypochlorite. This serves to convert the mercaptan to the sulfonyl chloride in a reproducibly good yield. The solubility of the product in the organic phase serves to protect it from hydrolysis to the sulfonic acid. Again, temperatures in the range of −20° C. to 25° C. are employed with temperatures in the range of −5° C. to 5° C. being most generally used.

SCHEME II



V VI

As an alternative, it is sometimes preferred to prepare sulfonyl chlorides of Formula IV from benzyl sulfides of Formula VI (Scheme II). Reaction conditions as described above for the conversion of mercaptans to sulfonyl chlorides are operable. This procedure yields by-products containing benzyl residues which are generally removed by washing the product with water and/or an appropriate organic solvent and drying in vacuo.

Compounds of general Formulae V or VI may be prepared by routes illustrated in Scheme III. Some derivatives of Formulae V and VI are known materials (i.e., V: X=Z=Me,Y=H and VI: X=Z=Me,Y=H) prepared by methods described in *J. Med. Chem.*, 25, 420 (1982). Compounds of Formula V are prepared directly by reaction of a 1,3-diketone with commercially available 3-amino-5-mercapto-1,2,4-triazole of Formula VII in glacial acetic acid as a solvent. Generally the reaction is performed at reflux. Alternatively, the compound of Formula VII may be benzylated with benzyl chloride using an alkali earth metal alkoxide (i.e., NaOH) as a base to yield the known benzyl sulfide of Formula VIII (*J. Heterocycl. Chem.*, 12, 1187 (1975)). The benzyl sulfide of Formula VIII can be condensed with not only 1,3-diketones but also β-keto esters, malonic esters, malonaldehyde, β-ketoaldehydes or α-formyl esters or derivatives thereof (i.e., acetals or enol ethers) to yield products of Formula VI as illustrated in Table A. Generally these reactions can be carried out under acidic conditions (i.e., glacial acetic acid as a solvent) or basic conditions (i.e., NaOR in ROH wherein R is C_1 to C_4 alkyl). In cases where the X, Y and Z substituents in Formula VI are derived from a 1,3 -diketone, compounds of Formula VI may be prepared by benzylation of NaOH) and benzyl chloride in a variety of solvents (i.e., water, methanol, ethanol, THF, dioxane, acetonitrile, DMF or DMSO or combinations of the aforementioned).

SCHEME III

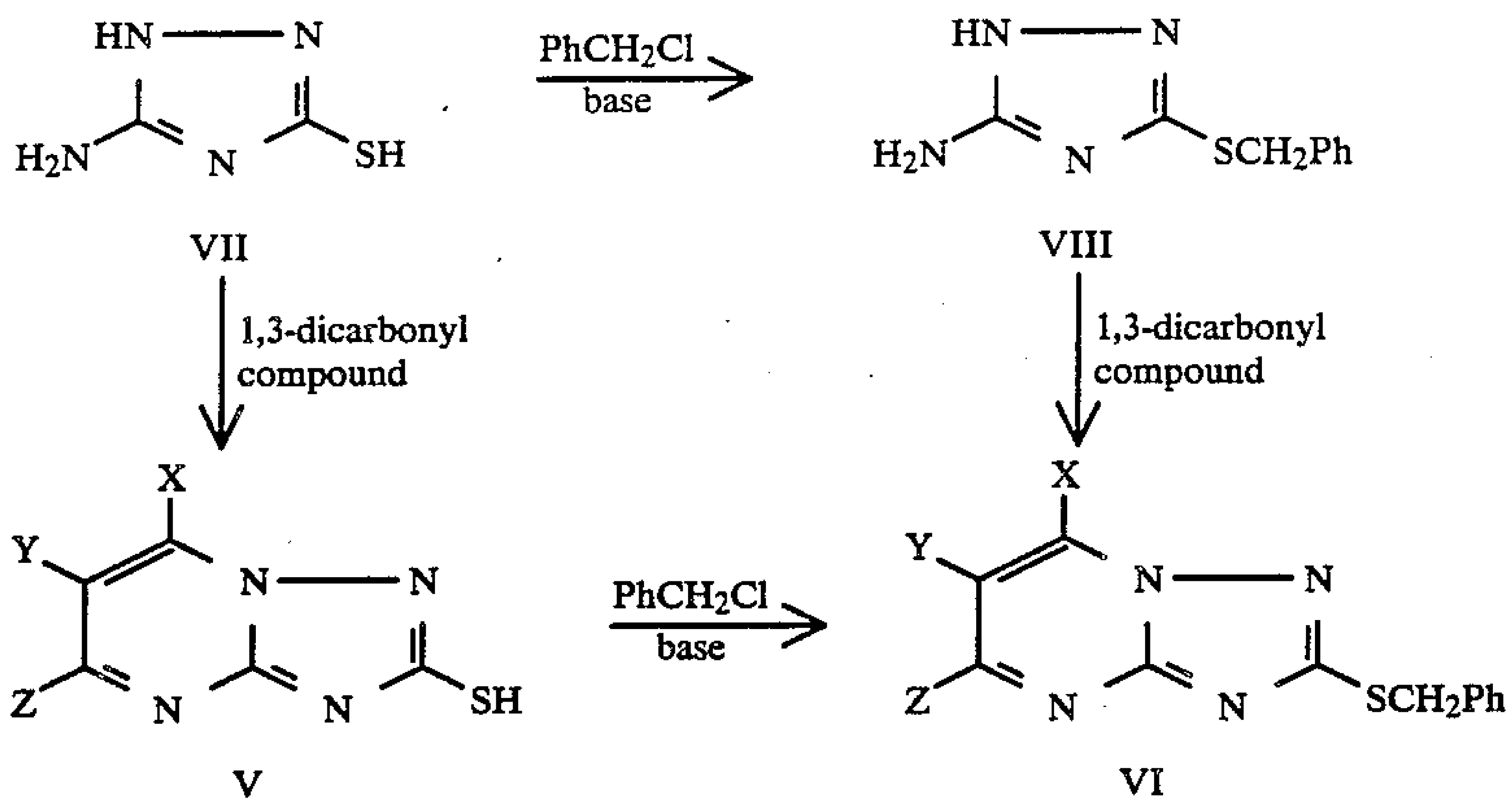
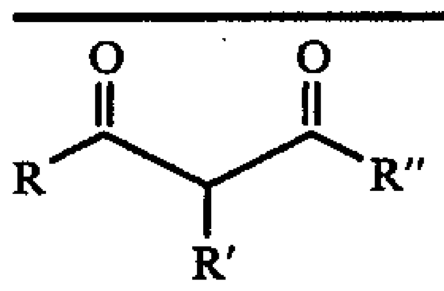
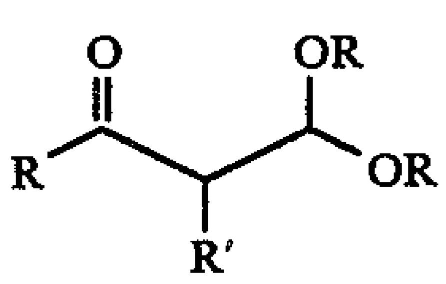
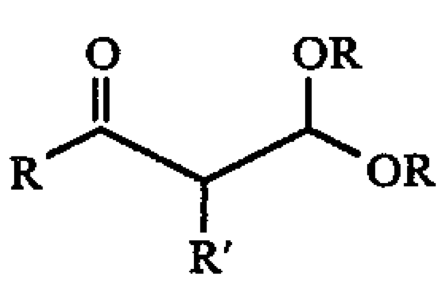
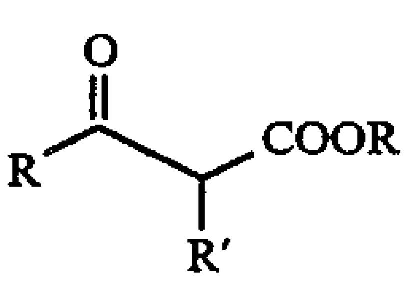
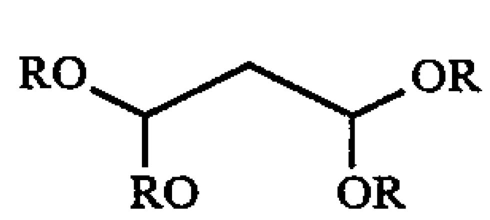
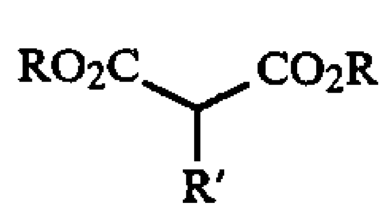


TABLE A

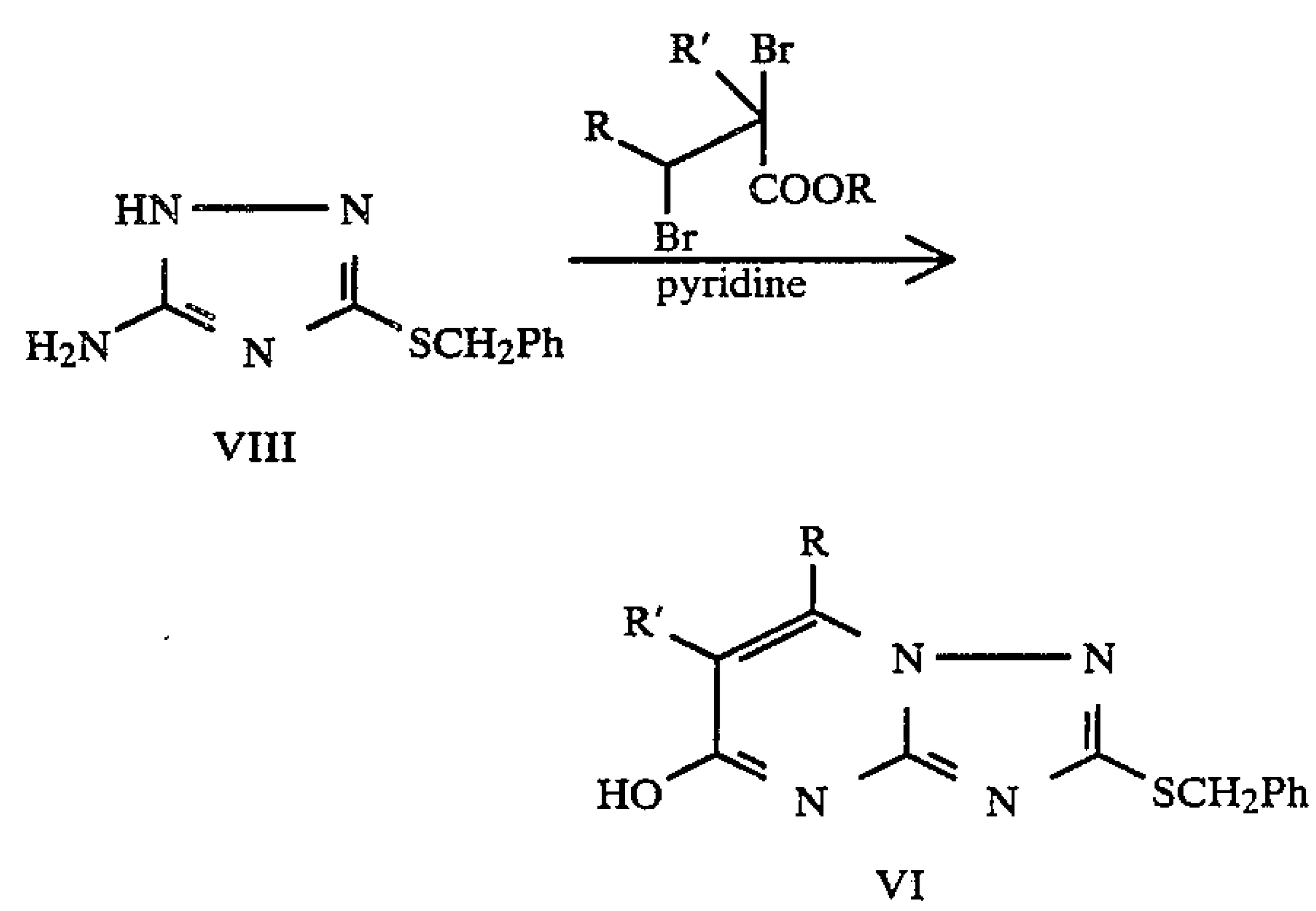
1,3-Dicarbonyl Compound or Derivative	Reaction Conditions	Compound of Formula V or VI X	Y	Z
	acid	R	R'	R"
	acid	H	R'	R
	base	R	R'	H
	acid	OH*	R'	R
	acid	H	H	H
	base	OH	R'	OH

*In this structural representation, as well as others bearing OH groups at 5- or 7-positions of the 1,2,4-triazolo[1,5-a]pyrimidine, the enol form has been depicted. Clearly this is the equilibrium with the various keto forms.

In instances where the 1,3-dicarbonyl compound is unsymmetrical, the possibility of obtaining two different isomers from condensation with Compound VIII exists. In general, under acidic conditions the exocyclic nitrogen in Compound VIII is the first to condense with the 1,3-dicarbonyl compound. Under basic conditions the endocyclic nitrogen in Compound VIII is sometimes more reactive. Consequently, in situations where a clear difference in reactivity of the two carbonyl functionalities in the 1,3-dicarbonyl compound exists, some measure of regiochemical control may be achieved by choice of reaction conditions (i.e., entries 2 and 3 in Table I).

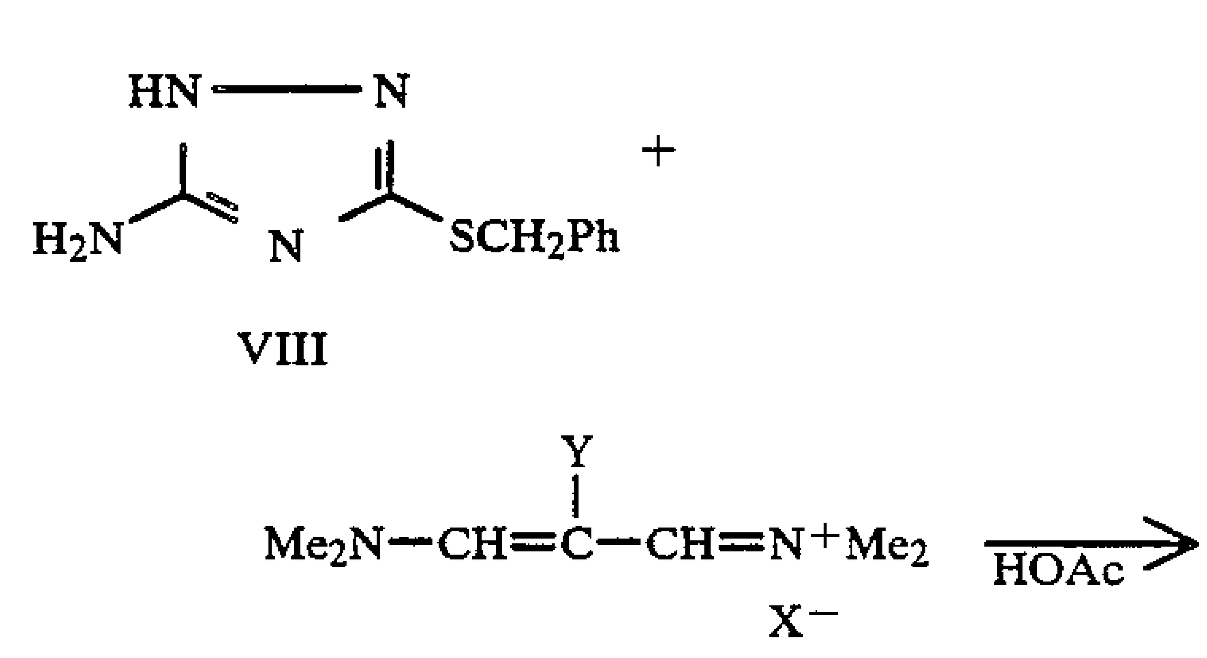
To prepare the alternative regioisomer to that depicted in entry 4 in Table A (i.e., VI: X=R, Y=R', and Z=OH) a route illustrated in Scheme IV was followed. Compound VIII was condensed with 2,3-dibromoalkylcarboxylic acid esters to yield a compound of Formula VI (VI: X=R, Y=R', Z=OH). The reaction is generally carried out in refluxing pyridine.

SCHEME IV



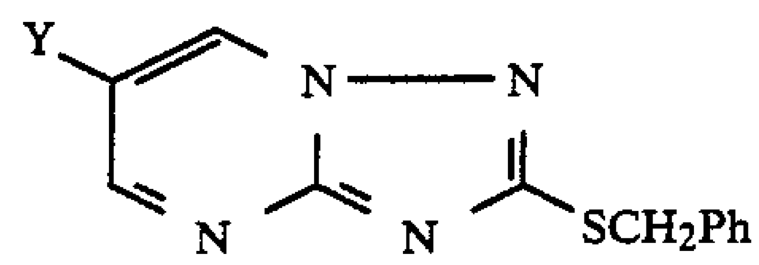
An additional route to compounds of Formula VI involves condensation of Compound VIII with methanaminium compounds of Formula IX as illustrated in Scheme V. The condensation is usually carried out by reaction in refluxing glacial acetic acid and is useful in the synthesis of a number of 6-substituted 1,2,4-triazolo[1,5-a]pyrimidines.

SCHEME V



-continued

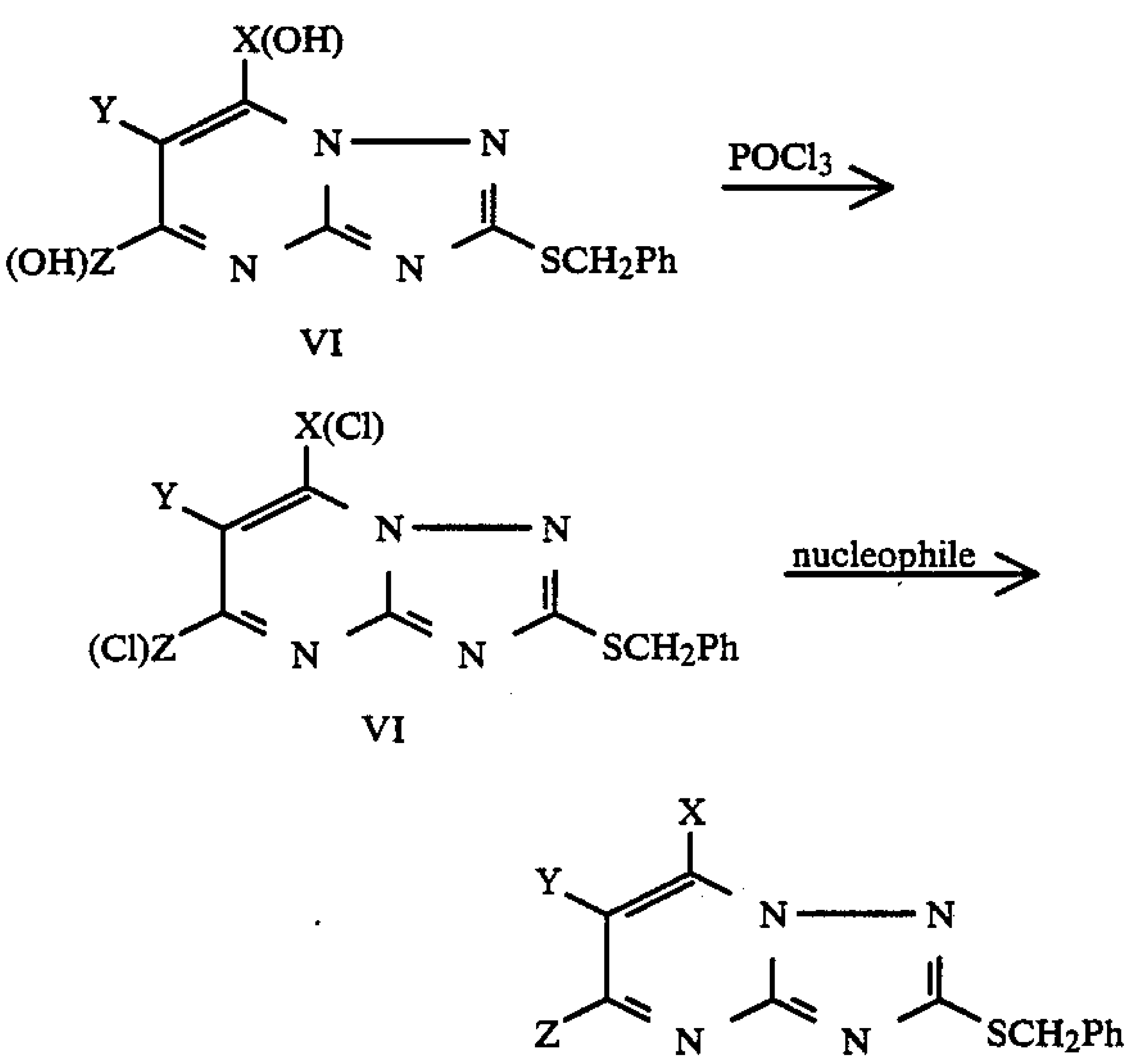
SCHEME V



VI

In the synthetic routes listed above, compounds of Formula VI where X and/or Z is OH are capable of undergoing further transformation (Scheme VI). For example, treatment of a compound of Formula VI (X and/or Z=OH) with phosphorus oxychloride yields the corresponding compound of Formula VI (X and/or Z=Cl). The reaction is generally carried out at reflux in neat phosphorus oxychloride or with phosphorous oxychloride in a solvent (i.e., acetonitrile). Compounds of Formula VI (X and/or Z=Cl) can be further reacted with nucelophiles (i.e., $NaOCH_3$, MeMgBr) to yield compounds of Formula VI (X and/or Z=OCH_3 or CH_3, respectively). In addition, compounds of Formula VI (X and/or Z=Cl) may be reduced to afford other compounds of Formula VI (X and/or Z=H). An effective reducing agent for this type of transformation is zinc-copper couple in the presence of acid.

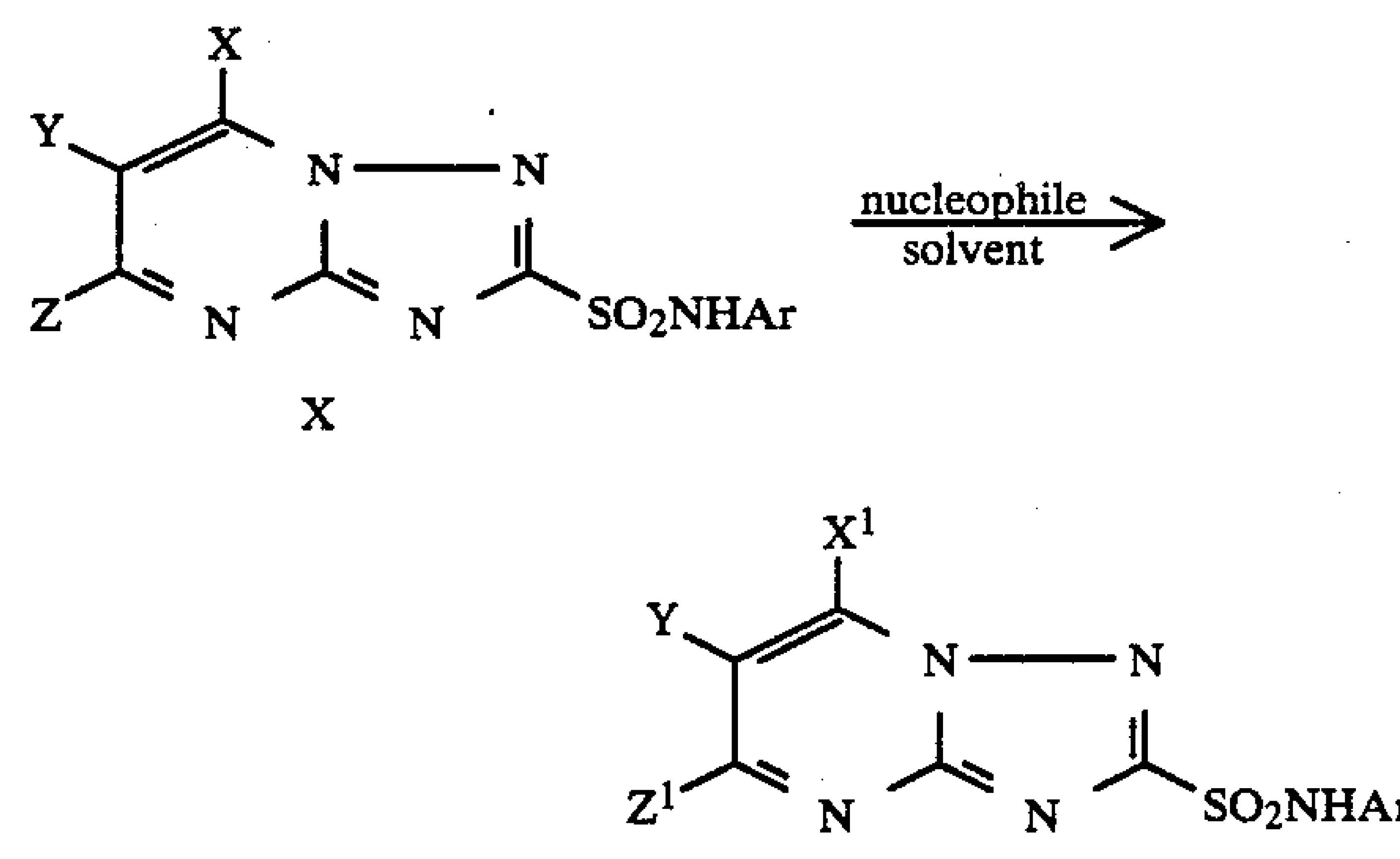
SCHEME VI



VI

Other compounds of the present invention are best prepared in a manner illustrated in Scheme VII. Compounds such as are represented by Formula XI wherein X^1 and Z^1 are independently represented by hydrogen, C_1-C_4 alkyl, alkylthio, arylthio, or amino (including mono- and disubstituted alkylamino), can be prepared by this method. The method involves the reaction of a compound of Formula X wherein X and Z independently represent hydrogen, C_1-C_4 alkyl or an appropriate leaving group with a nucleophile in a suitable solvent. This procedure effects the substitution of the leaving group by the nucleophilic unit. A representative leaving group that is effective in this process is trifluoroethoxide ($^{-}OCH_2CF_3$). Representative nucleophiles for this process include alkali metal salts of alkyl mercaptans, alkali metal salts of aryl mercaptans, ammonia, primary and secondary alkylamines, and alkali metal salts of hydroxides. These nucleophiles result in the displacement of the leaving group (X and/or Z) in Formula X to produce a compound of Formula XI containing X^1 and/or Z^1 represented as alkylthio, arylthio, amino, mono- and disubstituted alkylamino, or hydroxyl, respectively. Suitable solvents for this transformation include polar aprotic solvents (i.e., DMSO, DMF), alcohols and water. Suitable reaction temperatures range from 0° C. to 100° C. although the temperature of the reaction is usually not critical. Reaction temperatures of 20° C. to 30° C. are most frequently employed.

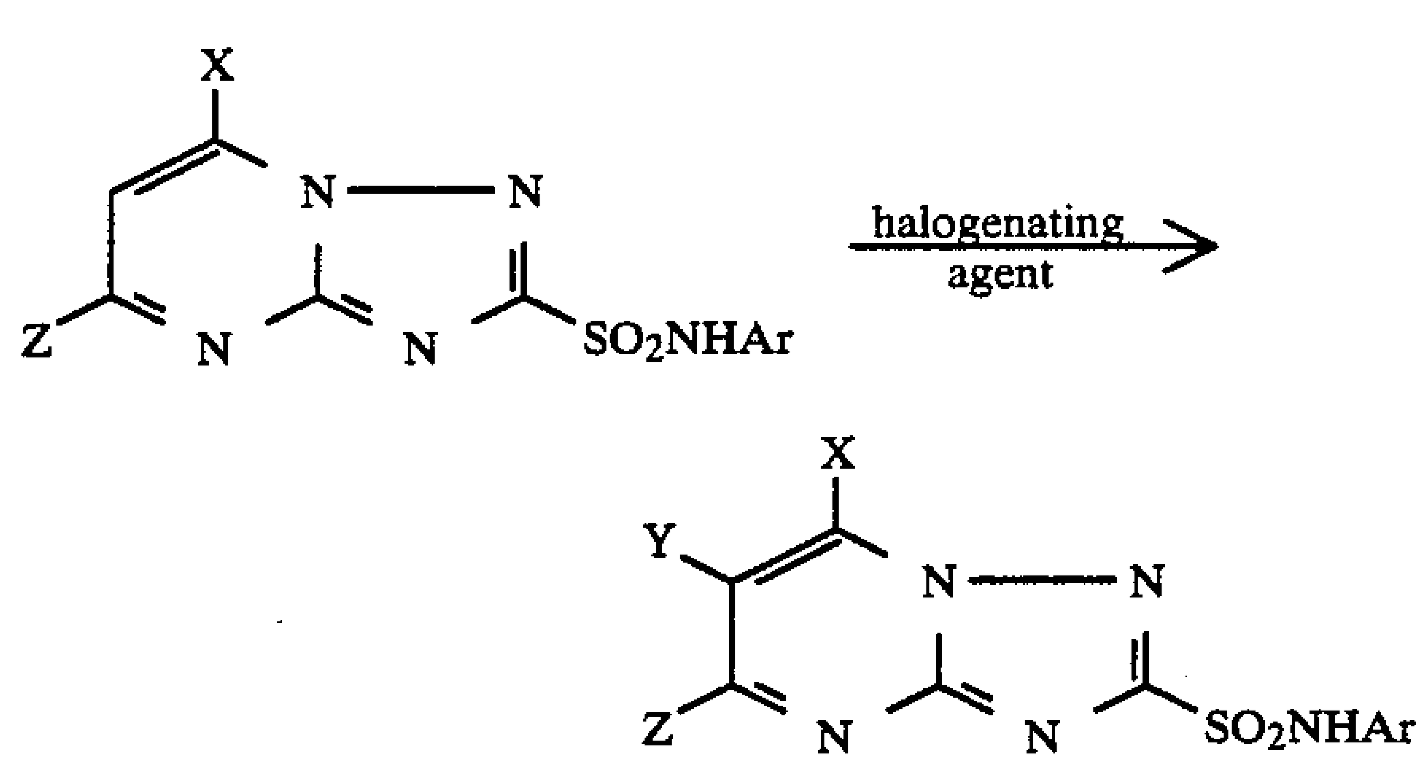
SCHEME VII



XI

In addition certain compounds of the present invention containing a halogen in the 6-position on the 1,2,4-triazolo[1,5-a]pyrimidine ring system may be prepared by halogenation of the corresponding 6-unsubstituted compound. This is illustrated in Scheme VIII. In general, N-halo-succinimide derivatives are the halogenating agents of choice. The reactions are often performed in acid solvents at temperatures ranging from room temperature to 150° C.

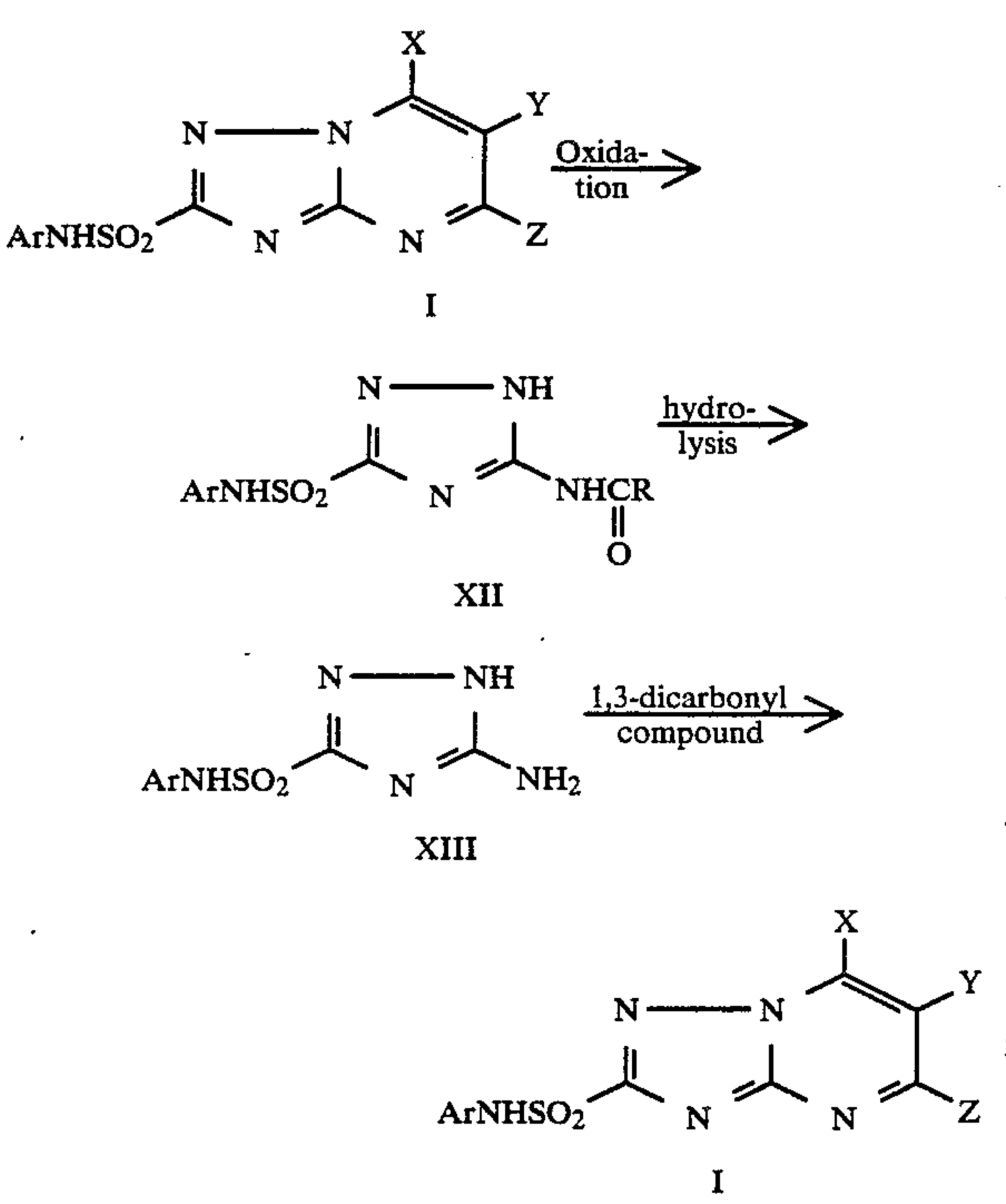
SCHEME VIII



Y = halogen

Another method to prepare the compounds of the present invention is illustrated in Scheme IX. Compounds of general Formula I can be oxidized to yield compounds of Formula XII. Oxidizing agents capable of this transformation include various transition metal oxidants such as derivatives of hexavalent chromium (Cr^{VI}) or heptavalent manganese (Mn^{VII}), organic peracids or peroxides. Oxidizing agents such as potassium permanganate, chromium trioxide, peracetic acid and hydrogen proxide are frequently employed. Preferred conditions for the conversion of compounds of Formula I to compounds of Formula XII involve reaction of the former with two to five molar equivalents of potassium permanganate in 0.1N to 1.0N aqueous alkali metal hydroxide (i.e., NaOH or KOH) as a solvent. The reaction may be run at temperatures ranging from ambient temperature to reflux. Most commonly the reaction is run at 50° C. to 60° C. The product of this reaction (Formula XII) can be hydrolyzed to a compound of Formula XIII by treatment with aqueous acid in an organic co-solvent. Typical acids include hydrochloric acid, sulfuric acid, acetic acid, trifluoroacetic acid or methanesulfonic acid. Appropriate organic co-solvents include acetone, methyl ethyl ketone, ethanol, acetonitrile or tetrahydrofuran. Lastly, compounds of Formula XIII can be reconverted to a compound of general Formula I by cyclization with a 1,3-dicarbonyl compound or an equivalent of a 1,3-dicarbonyl compound. The conditions for this cyclization, the structural requirements for the 1,3-dicarbonyl compound or an equivalent and structural considerations for the product are as described previously for the conversion of compounds of Formulae VII and VIII to compounds of Formula V and VI.

SCHEME IX



The method for the preparation of compounds of Formula I as illustrated in Scheme IX is employed advantageously in certain situations. Varius functional groups present on the 1,2,4-triazolo[1,5-a]pyrimidine ring system (X, Y and Z) of Formula I which impart useful herbicidal activity can only be produced in low yield by previously described routes. The primary cause for the low yield in the previously described routes is the incompatability of the function group or the ring system which bears the functional group to the conditions required to form the required sulfonyl chlorides of Formula IV. Examples of substituents (X, Y and Z) present in compounds of Formula I which are advantageously prepared by the method outlined in Scheme IX include H, halo (F, Cl, Br and I), hydroxy, C_1–C_4 alkyl, C_1–C_4 alkoxy, C_1–C_4 alkylthio, C_1–C_4 alkylsulfinyl, C_1–C_4 alkylsulfonyl, C_1–C_4 mono- or polyhaloalkyl, C_1–C_4 mono- or polyhaloalkoxy, C_1–C_4 polyhaloalkylthio, C_1–C_4 polyhaloalkylsulfinyl, C_1–C_4 polyhaloalkylsulfonyl, amino, C_1–C_4 mono- or dialkylamino, phenyl, substituted phenyl, phenoxy, substituted phenoxy, phenylthio, phenylsulfinyl, phenylsulfonyl, substituted phenylthio, substituted phenylsulfinyl, substituted phenylsulfonyl, carboxyl, and carboxyl derivatives such as esters derived from C_1–C_4 alcohols. The substituents X and Y or Y and Z can also be joined to form a ring containing a total of five to seven atoms. This ring may contain heteroatoms (i.e., nitrogen, oxygen or sulfur), unsaturation (i.e., —CO— or —C═C—) or a halogen substituent.

The compounds of Formula I which are most advantageously prepared by the method outlined in Scheme IX contain substituents (X, Y and Z) which are one or more of the following: H, halo (F, Cl, Br and I), C_1–C_4 alkyl, C_1–C_4 alkoxy, C_1–C_4 alkylthio, C_1–C_4 alkylsulfinyl, C_1–C_4 alkylsulfonyl, C_1–C_4 mono or polyhalogalkyl, C_1–C_4 mono- or polyhaloalkoxy, C_1–C_4 polyhaloalkylthio, C_1–C_4 polyhaloalkylsulfinyl, C_1–C_4 polyhaloalkylsulfonyl, amino and C_1–C_4 mono- or dialkylamino.

Specifically preferred substituent patterns of Formula I which may be prepared by the method outlined in Scheme IX are the following:

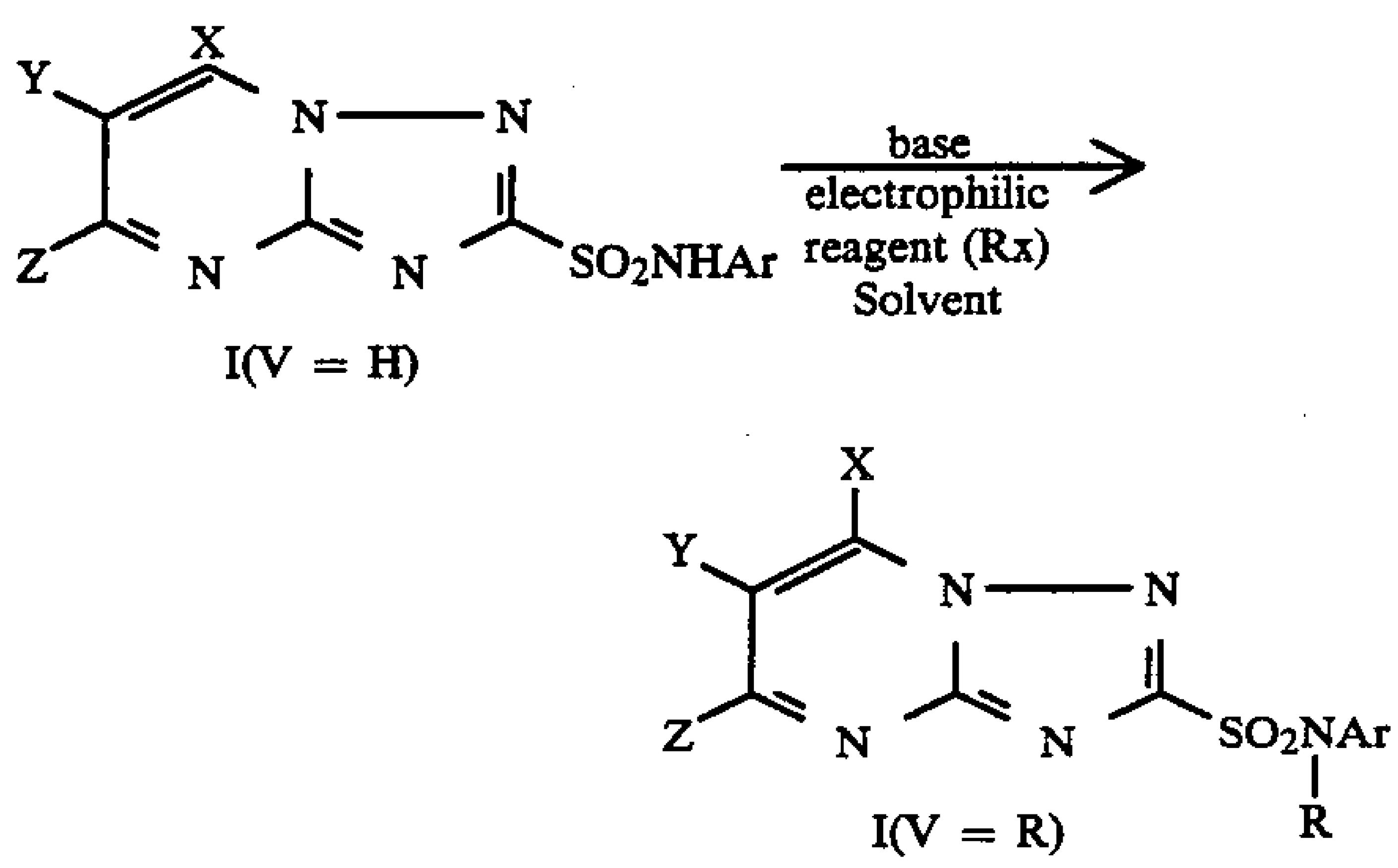
1. X═Y═Z═H
2. X═CF_3, Y═H and Z═CH_3
3. X═Z═CF_3 and Y═H
4. X═Cl, Y═H and Z═CH_3
5. X═OCH_3, Y═H and Z═CH_3
6. X═OC_2H_5, Y═H and Z═CH_3
7. X═SCH_3, Y═H and Z═CH_3

The starting material of Formula I in the reaction sequence of Scheme IX may contain one or more of the following substituents: H, halo (F, Cl, Br and I) and C_1–C_4 alkyl. The aromatic ring in these starting materials and intermediates is defined as described previously for Formula I. The R group in intermediates of Formula XII may be H or CH_3.

Compounds of the present invention represented by Formula I wherein V is R are derived from compounds represented by Formula I wherein V is H as illustrated in Scheme X. The derivatization procedure involves treatment of compounds of Formula I wherein V is H with a base in a suitable solvent followed by the introduction of an appropriate electrophilic derivatizing reagent. From this process compounds of Formula I wherein V is R can be isolated in good yields. Suitable bases include tertiary alkylamines (i.e., triethylamine), pyridine, 4-dimethylaminopyridine, alkali metal carbonate (i.e., sodium carbonate or potassium carbonate) and alkali metal alkoxides (i.e., sodium ethoxide or potassium t-butoxide). Suitable solvents include ethers (i.e., tetrahydrofuran), pyridine, acetone, acetonitrile, alcohols (i.e., methanol, ethanol, isopropanol and t-butanol) and polar aprotic solvents (i.e., DMSO and DMF). Suitable electrophilic reagents include alkyl halides, arylalkyl halides (i.e., benzyl chloride), carboxylic acid chlorides, alkyl chloroformates, aryl chloroformates, N,N-dialkylcarbamoyl chlorides, alkylsulfonyl chlorides arylsulfonyl chlorides, alkyl chlorothioformates

and aryl chlorothioformates

SCHEME X



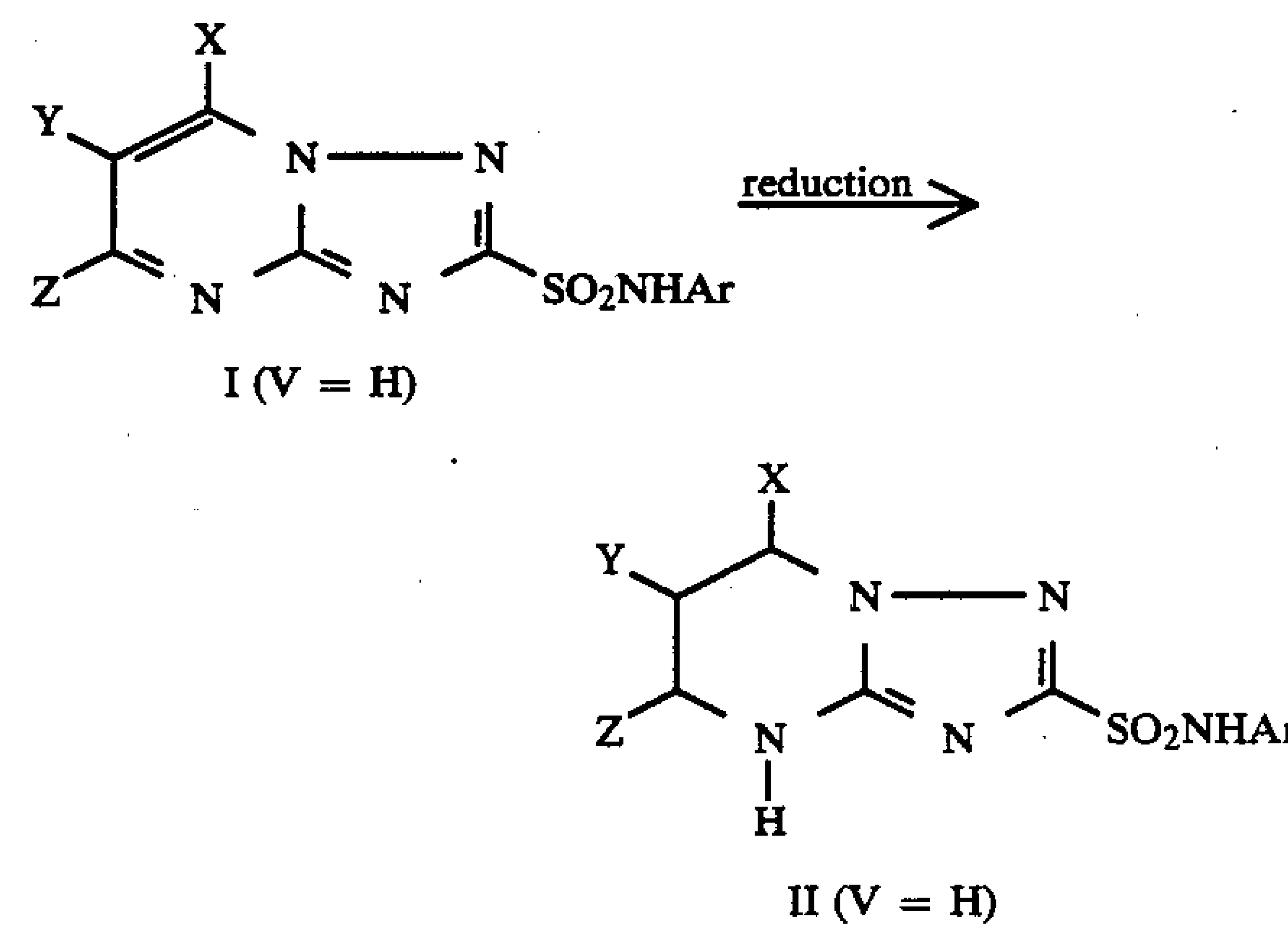
Agriculturally acceptable salts of the compounds of Formula I can be prepared by treatment of compounds of Formula I with a metal hydroxide such as sodium hydroxide, potassium hydroxide, or magnesium hydroxide, or an amine such as ammonia, dimethylamine, triethylamine, triethanolamine, diallylamine, 2-butoxyethylamine, morpholine, cyclododecylamine, or benzylamine. The reactions are typically carried out in a solvent in which one or more of the compounds of Formula I, the base, and the agriculturally acceptable salt product has appreciable solubility. Water is a preferred solvent. The agriculturally acceptable salts can be recovered from the reaction mixtures obtained by conventional means such as filtration or evaporation of the volatile components, or the reaction mixtures can be used without isolation.

In typical operations, a compound of Formula I is placed in water or other suitable solvent and an approximately equimolar quantity or an excess of base is added. The solution obtained is combined with agriculturally acceptable adjuvants and used as a herbicide.

The salts of this invention are additionally useful for purifying the compounds of Formula I. In typical operations, a contaminated compound of Formula I is combined with an excess of base in water to obtain a solution of the salt. Water insoluble contaminants are then removed by filtration or extraction with an immiscible organic solvent, such as methylene chloride or ether, and the compound of Formula I is regenerated by the addition of an acid and recovered by filtration, centrifugation, or the like. Sodium hydroxide and ammonium hydroxide are preferred bases and hydrochloric acid a preferred acid in these procedures.

Compounds of the present invention represented by Formula II are also derived from compounds represented by Formula I as illustrated in Scheme XI. the general process involves the reduction of compounds of general Formula I with an appropriate reducing agent in a suitable solvent to yield compounds of general Formula II. Reducing agents which are effective include metal hydrides (i.e., sodium borohydride) in the presence of acids (i.e., methanesulfonic acid) and hydrogen in the presence of a normal hydrogenation catalyst (i.e., palladium on carbon). For reductions with metal hydrides, polar aprotic solvents (i.e., DMSO) are most frequently used. For reductions using hydrogen and a catalyst, alcohols (i.e., ethanol) are most frequently employed as solvents.

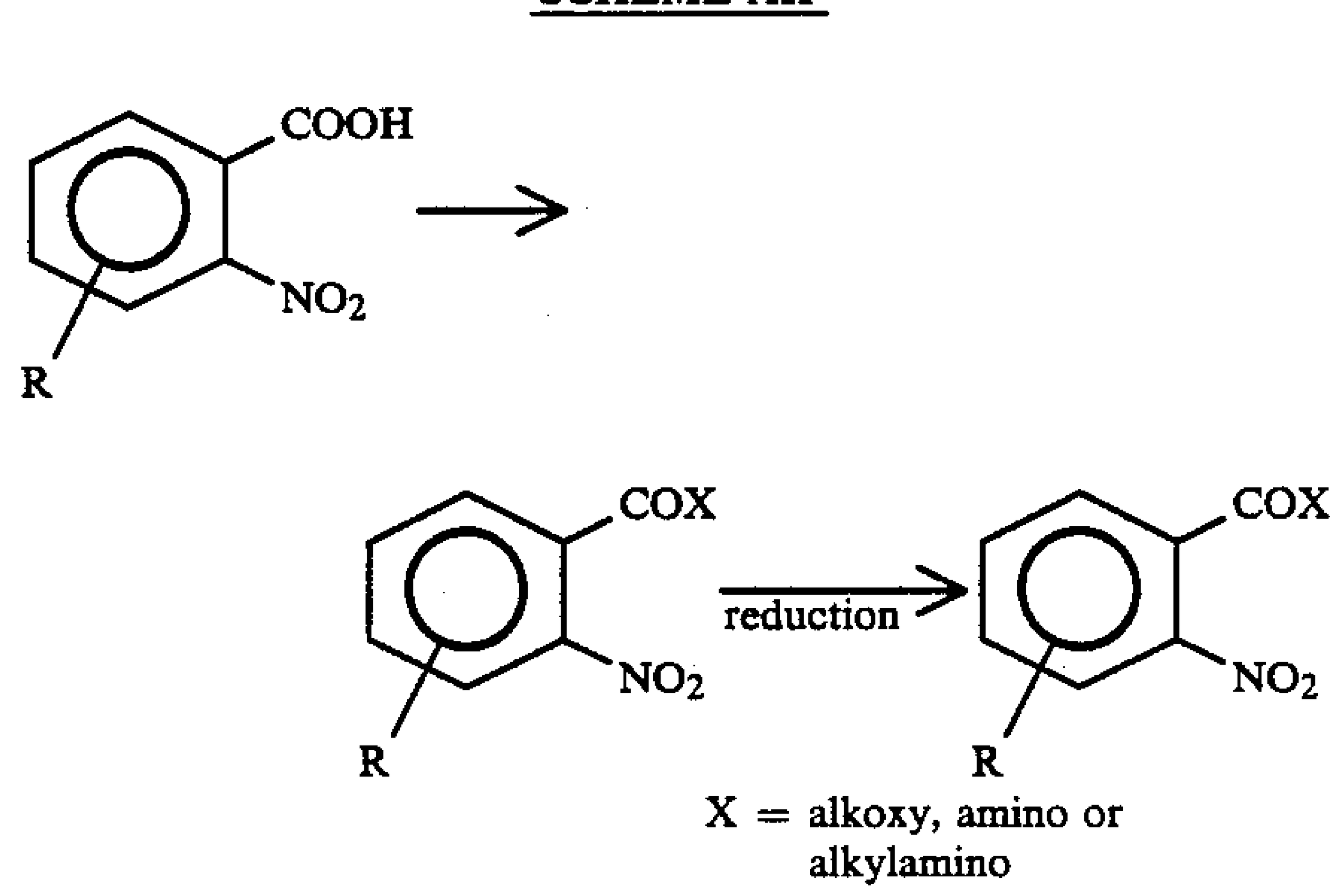
SCHEME XI



The majority of the amino compounds ($ArNH_2$) utilized to prepare the compound of the present invention as illustrated in Scheme I were obtained from commercial sources or prepared by known literature procedures or minor modifications of literature procedures. Others are novel compounds made by novel processes.

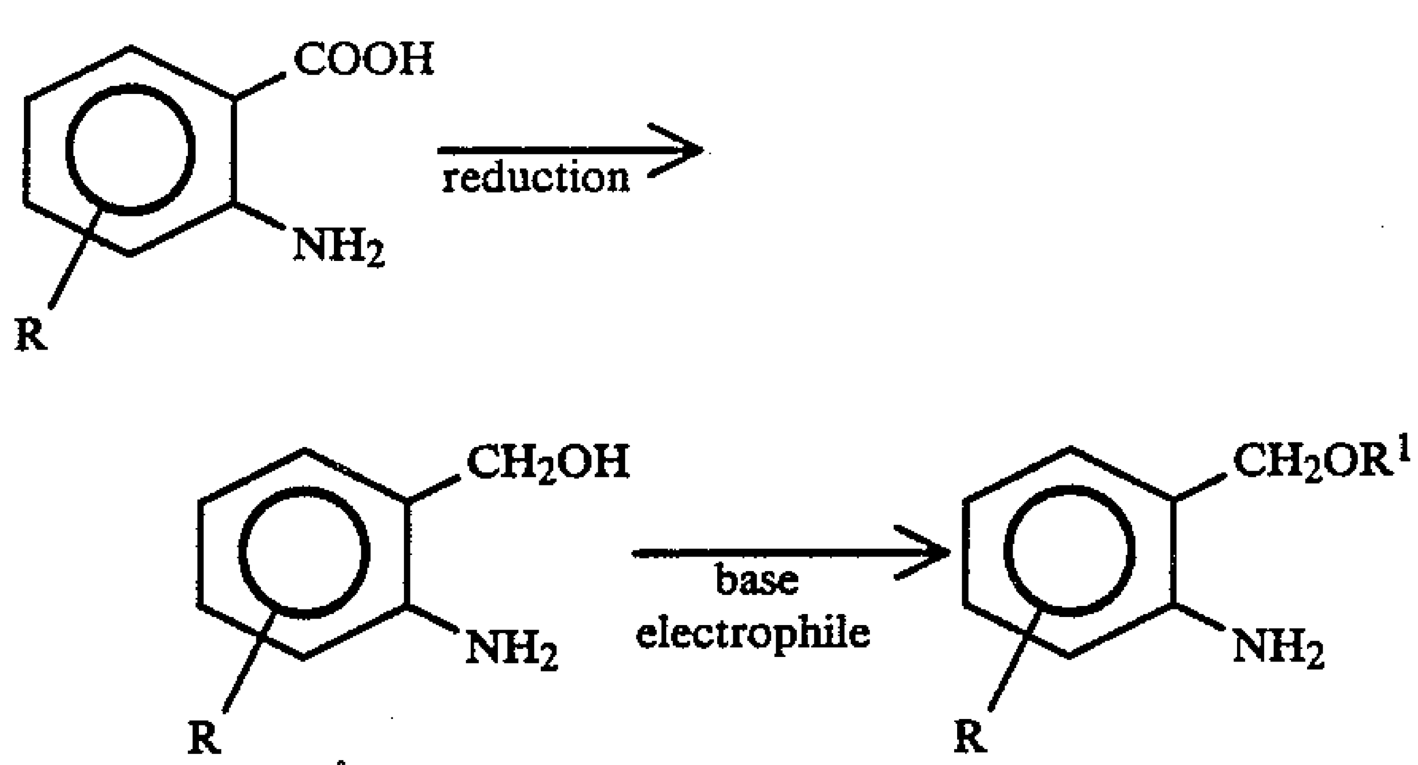
A number of the amino compounds ($ArNH_2$) used to prepare the compounds of the present invention are derivatives of anthranilic acid. Many of these compounds can be prepared according to conventional methods described by S. J. Holt et al., *Royal Soc. Proc. Sec. B,* 148, 481 (1958), P. W. Sadler et al., *J. Am. Chem. Soc.,* 78, 1251 (1956), and G. Reissenweber et al., U.S. Pat. No. 4,310,677 (1982). Other anthranilic acid derivatives can be prepared by standard derivatizations (i.e., conversion to esters and amides) of known substituted or unsubstituted 2-nitrobenzoic acids followed by reduction of the nitro group as represented in Scheme XII.

SCHEME XII



A number of the amino compounds are prepared by reduction of anthranilc acids or esters and subsequent derivatization of the reduction product. This is outlined in Scheme XIII. The carbinol reduction products may be derivatized by reaction with base and various electrophiles (i.e., alkyl halides and carboxylic acid chlorides).

SCHEME XIII



$R^1 = C_1$–C_4 alkyl or C_1–C_4 acyl

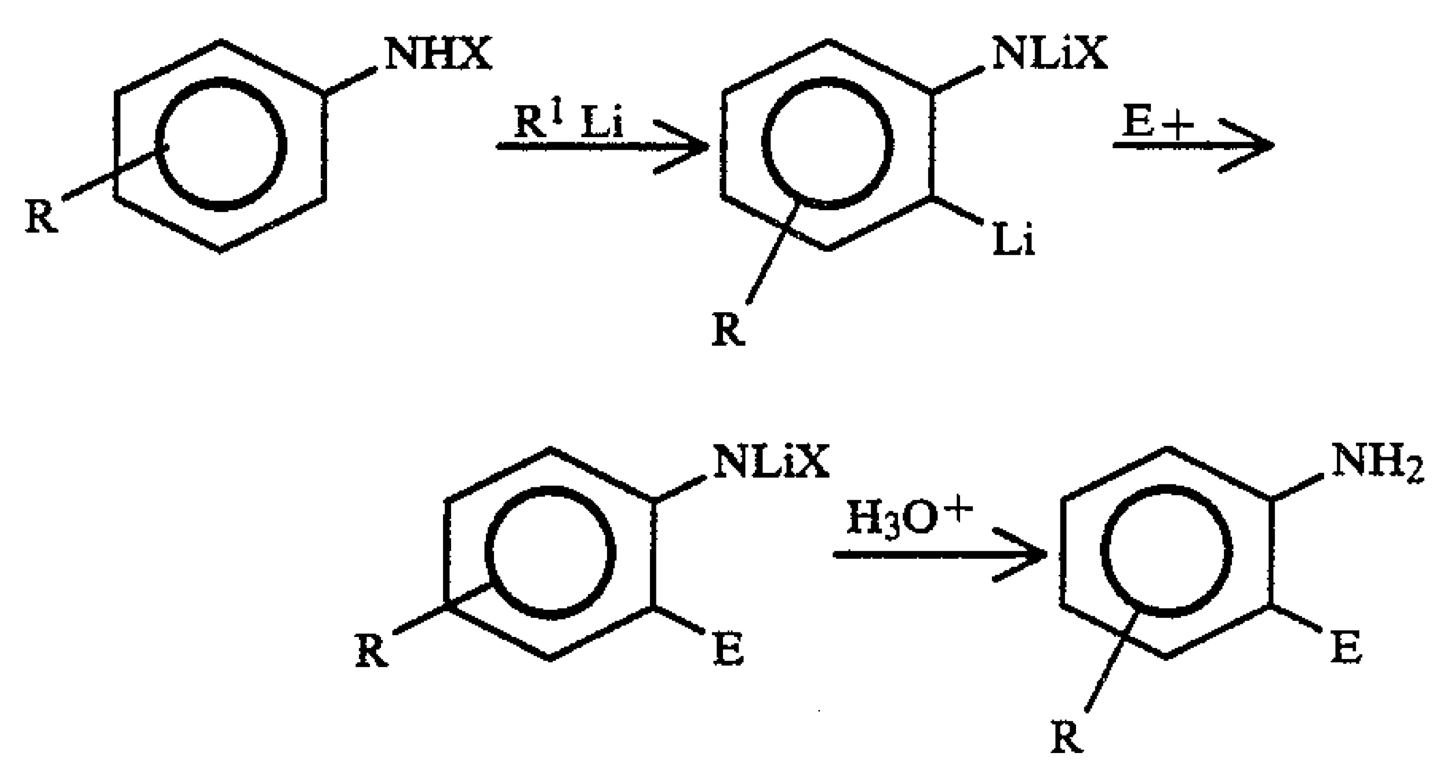
A large number of the amino compounds utilized in the preparation of the compounds of this invention contain halogen substituents ortho to the amino group. Many of these compounds were prepared by halogenation of the corresponding material bearing no substituent in the ortho position according to a general procedure described by R. S. Neale et al., *J. Org. Chem.*, 29, 3390 (1964). The starting materials for these halogenations are commercially available or known in the literature (i.e., British Pat. No. 695,164 (1953); D. S. Noyce et al., *J. Org. Chem.* 26, 1732 (1961) and U.S. Pat. No. 3,813,234 (1974)). In certain instances to facilitate the transformation and insure ortho selectivity in the halogenation process the starting materials for the halogenation were acetamide derivatives ($ArNHCOCH_3$) or derivatives containing groups (i.e., Br) which would block halogenation at other positions in the molecule (i.e., para to the amino group). Following halogenation the acetamide derivatives were hydrolized back to the desired amino compound and the blocking groups were removed (i.e., Br in the para position was selectively removed by reduction in the presence of Cl in the ortho position). Other chlorine and bromine substituted amino compounds were prepared by known procedures (i.e., U.S. Pat. No. 4,188,342 (1980); C. R. Rasmussen et al. *J. Med. Chem.*, 21, 1044 (1978); H. E. Dadswell et al. *J. Chem. Soc.*, 1102 (1927); U.S. Pat. No. 3,813,234 (1974) and P. B. D. DeLaMare and J. H. Ridd, "Aromatic Substitution, Nitration and Halogenation", Academic Press, New York (1959), p. 106.

A number of the amino compounds used as starting materials for the compounds of this invention contain sulfur substituents in the ortho position. These were prepared using known procedures (i.e., R. R. Gupta et al *Heterocycles,* 16, 1527 (1981) and J. P. Chupp et al., *J. Org. Chem.*, 49, 4711 (1984)). In some cases alkylthio groups were present and these were synthesized by alkylation of the corresponding mercaptan. Compounds having alkyl or aryl sulfinyl or sulfonyl groups were synthesized by oxidation of the appropriate alkyl or arylthio groups.

Some starting amino compounds containing amino, alkylamino, aryloxy or pyridyloxy groups were prepared by catalytic reduction of the corresponding nitro compounds. The amino, alkylamino, aryloxy or pyridyloxy group were usually introduced via displacement of a leaving group ortho to the nitro group in the requisite nitrobenzene.

Other starting amino compounds were prepared by procedures involving metalation of the aromatic ring of N-substituted derivatives (i.e., t-butoxycarbonyl derivatives) of an aromatic amino compound followed by the resulting organometallic reagent with an electrophile. This general procedure is described in H. Gschwend, *Org. Reactions,* Vol. 20, 1–360 (1979) and is outlined in Scheme XIV. Suitable metalating agents are organolithium reagents (i.e., n-butyl lithium or t-butyl lithium). Typical electrophiles include alkyl halides (i.e., methyl iodide, ethyl iodide), aldehydes (i.e., formaldehyde, acetaldehyde), ketones (i.e., acetone), alkyl or aryl sulfonyl halides (i.e., methylsulfonyl chloride), and dialkyl or diaryl disulfides (i.e., dimethyl disulfide). These electrophiles are useful for the introduction of alkyl, hydroxyalkyl and alkylthio and arylthio groups to the position ortho to the amino group. After the reaction of the organometallic intermediate with the electrophile the nitrogen substituent is removed by hydrolysis.

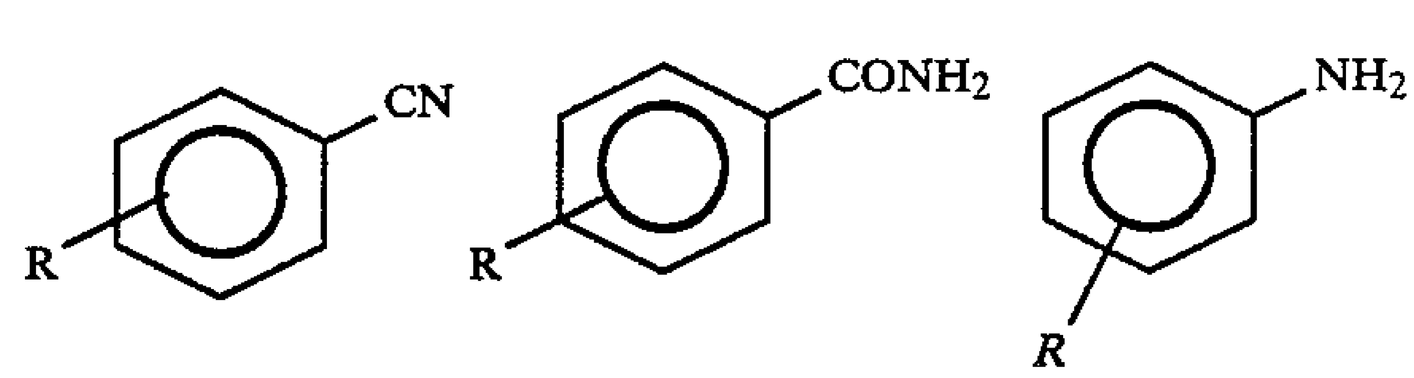
SCHEME XIV



e.q. X = COOtBu

Other aromatic amino compounds used to prepare compounds of the present invention are prepared by conversion of carboxylic acid groups or derivatives of carboxylic acid groups to amino groups by standard methodology. Such a transformation is illustrated in Scheme XV and described in *J. Royal. Netherlands Chem. Soc.*, 97, 53 (1978).

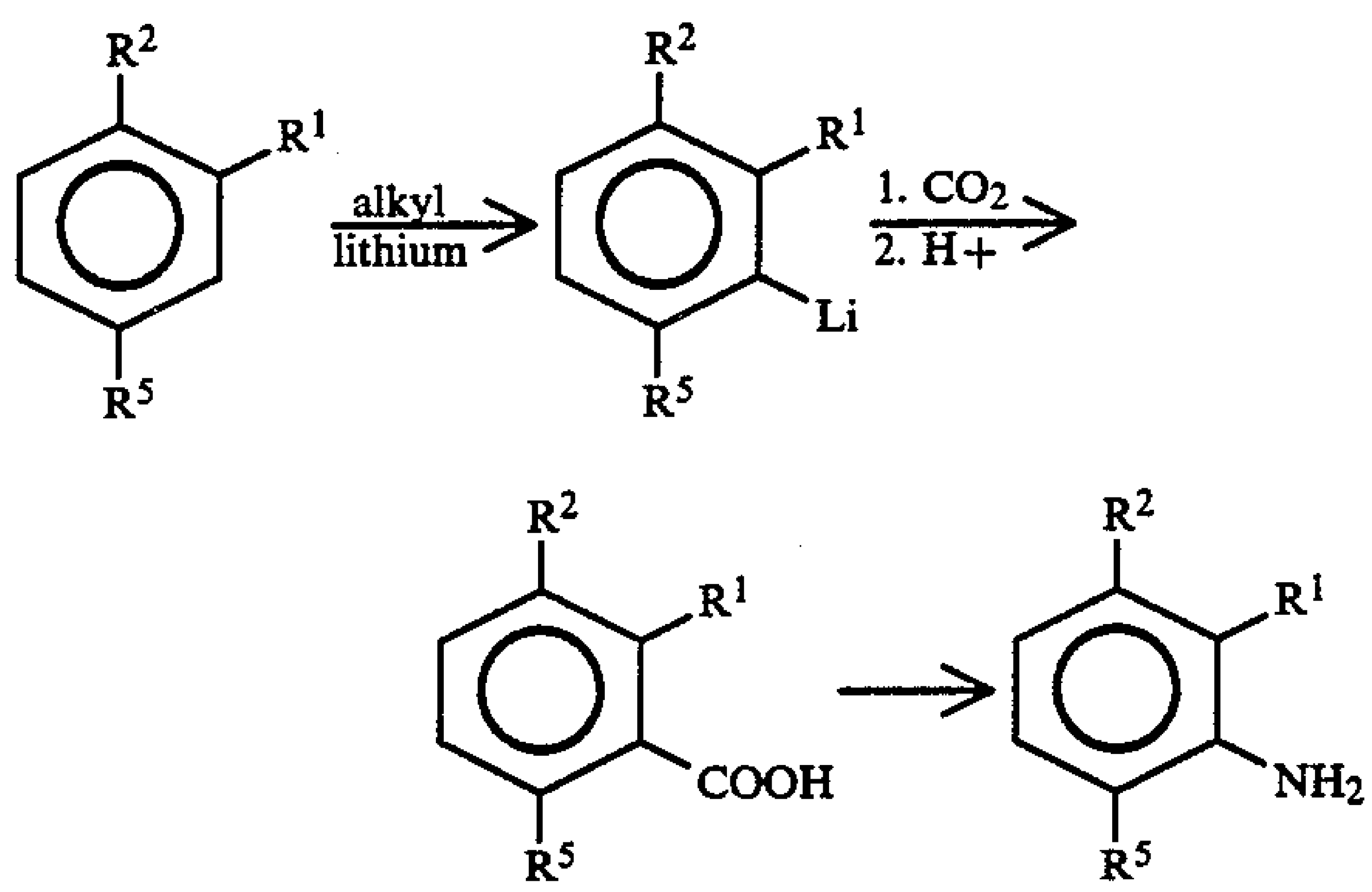
Scheme XV



Other amino compounds such as those which are heteroaromatic amino compounds are prepared by known procedures such as those described in *Rec. Trav. Chim.*, 69, 673 (1950), T. Talik et al., *Chem. Abstracts,* 59: 8698a (1963) and L. C. Behr and R. Fusco In "*Heterocyclic Compounds*", A. Weissberger, Ed. Vol 22, Interscience Publishers, New York (1967), pp. 3–174 or straightforward modification of the art described above.

Other amino compounds used to prepare compounds of the present invention are prepared by direct metalation of the aromatic ring. This is illustrated schematically in Scheme XVI. An aromatic ring bearing one to three substituents on the ring may be metalated with an alkyl lithium reagent (i.e. n-butyl lithium, s-butyl lithium or t-butyl lithium) to form an aryl lithium intermediate. This reaction is most frequently carried out in an ethereal solvent (i.e. diethyl ether, tetrahydrofuran or 1,2-dimethoxyethane) at temperature ranging from 78° C. to ambient temperature. It is sometimes advantageous to perform the metalation reaction in the presence of additives such as tetramethylethylenediamine. The aryl lithium reagent is generated in situ and is reacted with carbon dioxide followed by protonation of the resultant carboxylate to form the carboxylic acid. The carboxylic acid can then be converted to the corresponding amino compound by standard methodology of the Hoffman, Curtius, Lossen and Schmidt reactions.

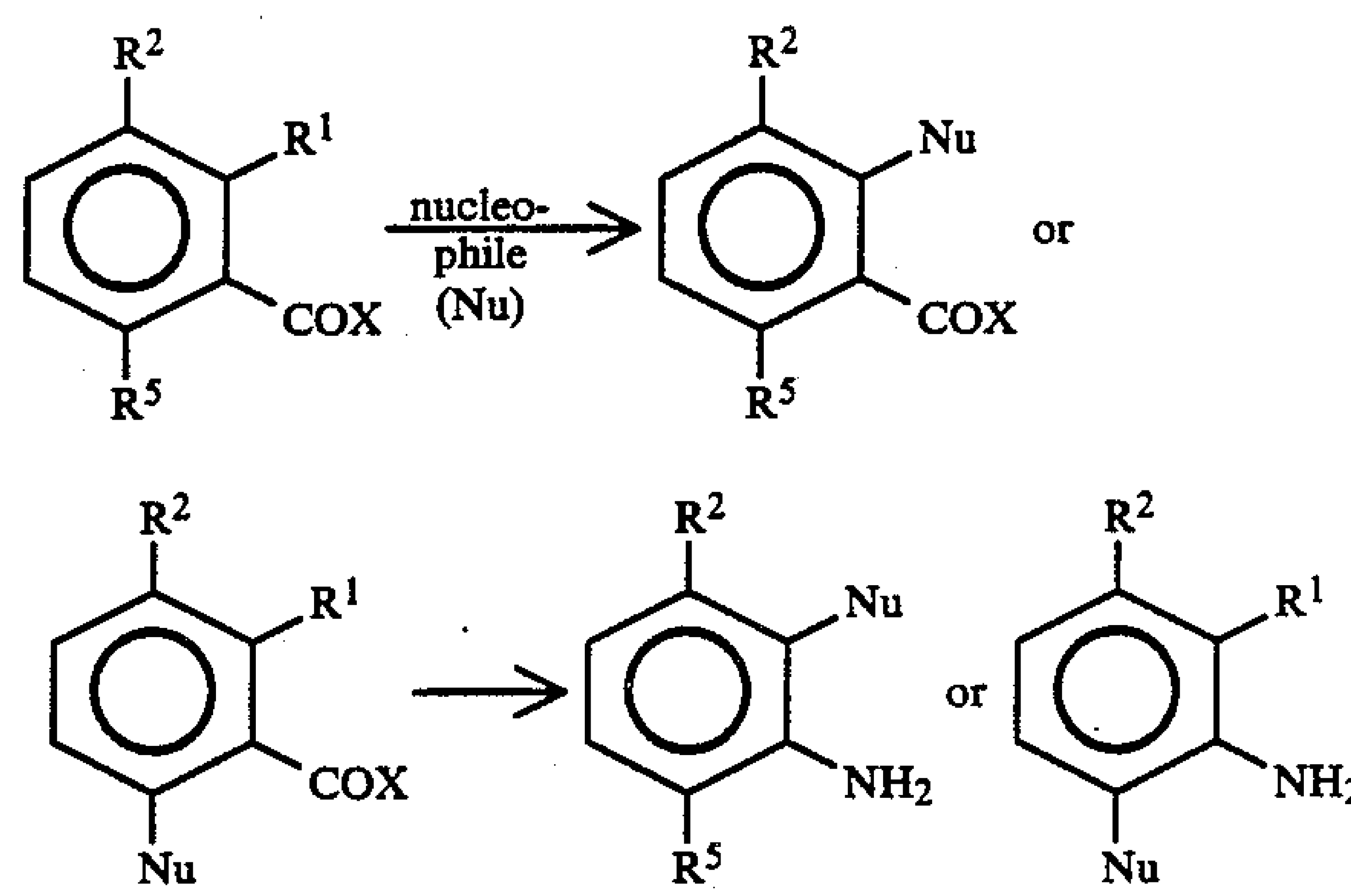
Scheme XVI



The substituents (R^1, R^2, and R^5) which are operable in the process illustrated in Scheme XVI are as follows: R^1, R^2, and R^5 may be chosen from among H, F, Cl, Br, I, C_1-C_4 alkyl, C_1-C_4 mono- or polyhaloalkyl or C_1-C_4 alkoxy. Most preferred substituents are R_2 is equal to H or C_1-C_4 alkyl; R^1 and R^5 are equal to F, Cl, C_1-C_4 mono- or polyhaloalkyl or C_1-C_4 alkoxy.

The intermediate carboxylic acid formed as illustrated in Scheme XVI or derivatives of the carboxylic acid (i.e. esters and amides) can be utilized to prepare other amino compounds which are useful in the preparation of compounds of Formula I of the present invention. This process is illustrated in Scheme XVII. When the carboxylic acid product contains a leaving group such as a F, Cl or Br atom at an adjacent position, the carboxylic acid may be converted to a suitable derivative and the halogen may then be replaced by displacement with a suitable nucleophile. Nucleophiles which are useful in this case include ammonia, C_1-C_4 monoalkylamines, C_1-C_4 dialkylamines, C_1-C_4 alkali metal alkoxides, C_1-C_4 alkali metal mono- or polyhaloalkoxides or C_1-C_4 alkali metal mercaptides. The use of these nucleophiles serves to replace the halogen substituent with amino, C_1-C_4 monoalkylamino, C_1-C_4 dialkylamino, C_1-C_4 alkoxy, C_1-C_4 mono- or polyhaloalkoxy or C_1-C_4 alkylthio respectively. The resultant products of the nucleophilic displacement can be converted to the corresponding amino compound by standard methodology of the Hoffman, Curtius, Lossen and Schmidt reactions.

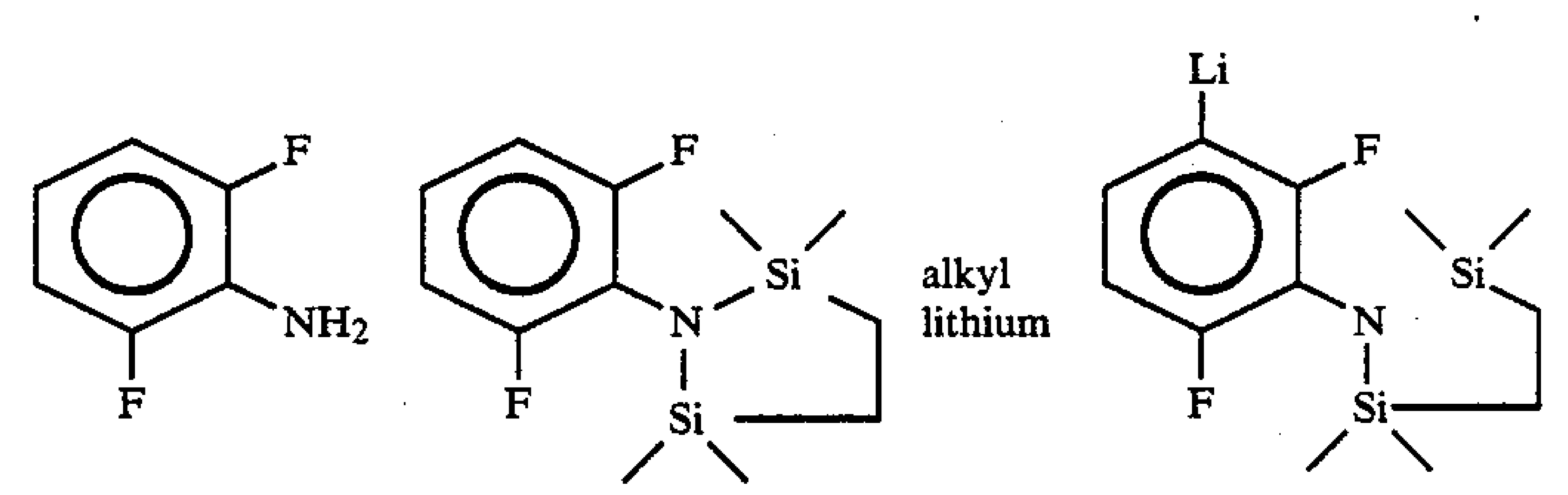
Scheme XVII



R^1 or R^3 = halogen and X = OH, OR*, or $N(R^*)_2$ where R* = H or C_1-C_4 alkyl.

Other amino compounds which are useful in the preparation of compounds of Formula I can be prepared as illustrated in Scheme XVIII. The starting material for this procedure is 2,6-difluoroaniline. The amino group of the aniline is protected with a silyl protecting group according to a general procedure described by Magnus et al. in *Tetrahedron Lett.*, 1787 (1981) and Guggenheim et al. in *Tetrahedron Lett.*, 1253 (1984). The protected aniline can then be metalated with an alkyl lithium reagent (i.e. n-butyl lithium, s-butyl lithium or t-butyl lithium) to form the corresponding aryl lithium reagent. The metalation is best carried out in ethereal solvents such as diethyl ether, tetrahydrofuran or dimethoxyethane at temperatures ranging from −78° C. to ambient temperature. It is sometimes advantageous to carry out the metalation in the presence of additives such tetramethylethylenediamine. The aryl lithium reagent is formed in situ and can be reacted with a variety of electrophilic reagents such as C_1-C_4 alkyl halides, C_1-C_4 dialkyl disulfides or C_1-C_4 alkyl sulfenyl halides, dimethylformamide, C_1-C_4 acyl halides or C_1-C_4 N-methyl-O-methyl alkylhydroxamates, C_1-C_4 alkyl chloroformates and carbon dioxide. These electrophilic reagents serve to introduce C_1-C_4 alkyl, C_1-C_4 alkylthio, formyl, C_1-C_4 acyl, C_1-C_4 alkoxycarbonyl and carboxyl groups, respectively, directly into the 3-position of the aromatic ring. The product from electrophilic substitution can be deprotected using standard methodology as described in the literature to form the desired amino compound.

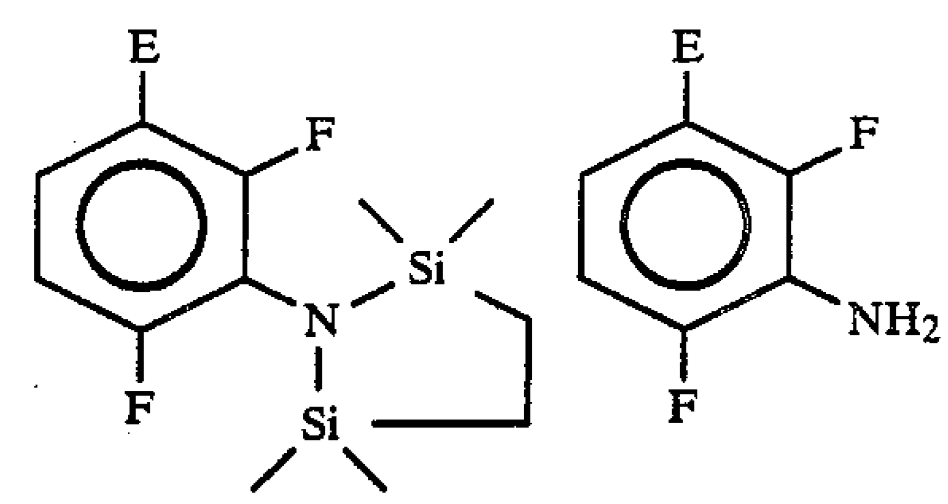
Scheme XVIII



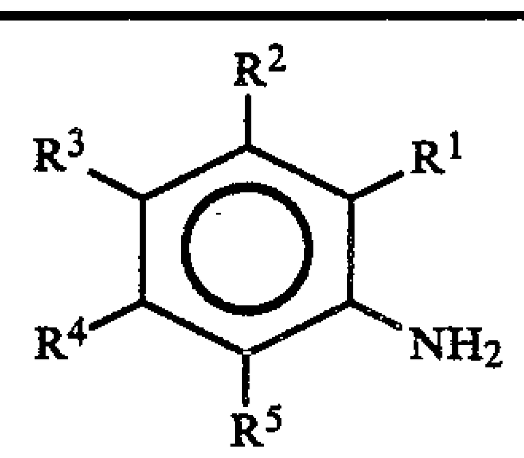
-continued

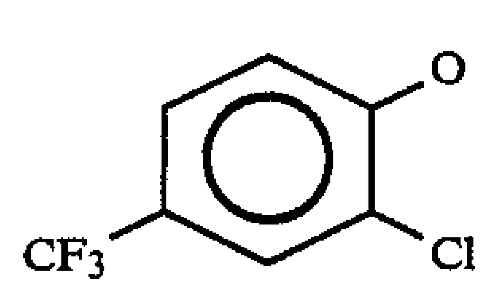
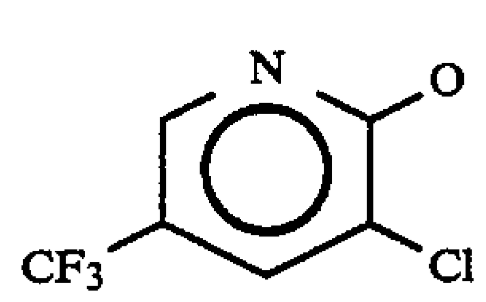
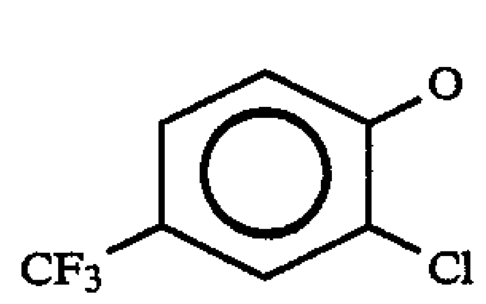
Scheme XVIII

electrophile

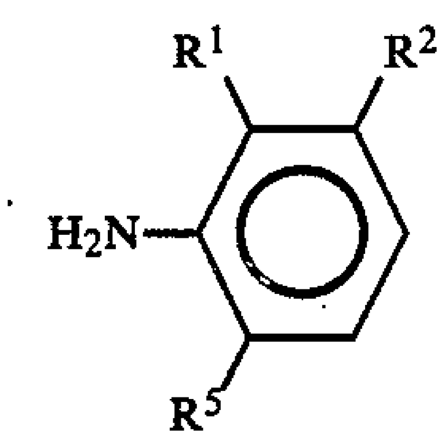


The table which follows contains a listing of some of the aromatic amino compounds prepared by methods described above and not previously described in known art, which compounds are useful in the preparation of the biologically active compounds of this invention.



Compound	R^1	R^2	R^3	R^4	R^5
A	Cl	$COOCH_3$	H	H	Cl
B	Br	$COOCH_3$	H	H	CH_3
C	CH_3	Cl	H	H	$COOCH_3$
D	Cl	CF_3	H	H	Cl
C	Cl	H	H	H	CH_2OCH_3
E	Cl	H	H	H	CH_2OAc
I	Cl	H	H	H	CH_2OCH_2Ph
J		H	H	H	H
K		H	H	H	H
L		H	H	H	F
M	F	H	H	H	SCH_3
N	CF_3	H	H	H	OCH_3
O	CF_3	H	H	H	$N(CH_3)_2$
P	CF_3	H	H	H	OCH_2CH_3
Q	CF_3	H	H	H	OCH_2CF_3
R	Br	CH_3	H	H	Br
S	Br	CH_3	H	H	Cl

The novel aniline compounds that are useful for the preparation of compounds of Formulae I and II can be described by the formula



wherein (1) R^1 represents CF_3, R^2 represents hydrogen, and R^5 represents C_1–C_4 alkoxy, C_1–C_4 polyfluoroalkoxy, or C_1–C_4 alkylthio; (2) R^1 and R^5 represent F and R^2 represents CH_3 or OCH_3; (3) R^1 and R^5 represent Cl and R^2 represents CO_2C_1–C_4 alkyl, or CF_3; (4) R^1 represents F, R^2 represents hydrogen, and R^5 represents C_1–C_4 alkylthio or 4-trifluoromethylphenoxy or 5-trifluoromethyl-2-pyridyloxy, each optionally containing up to two fluoro, chloro, or bromo substituents; (5) R^1 represents Cl, R^2 represents hydrogen, and R^3 represents hydroxymethyl, C_1–C_4 alkoxymethyl, C_1–C_4 alkanoyloxymethyl, or benzyloxymethyl; (6) R^2 and R^5 represent hydrogen and R^1 represents 4-trifluoromethylphenoxy or 5-trifluoromethyl-2-pyridyloxy, each optionally containing up to two fluoro, chloro, or bromo substituents, (7) a C_1–C_4 alkyl 3-amino-2-bromo-4-methylbenzoate; and (8) a C_1–C_4 alkyl 4-chloro-3-methylanthranilate.

Using the routes illustrated above or minor variations based on the principles illustrated above the novel compounds of this invention can be prepared.

The invention is further illustrated by the following examples.

EXAMPLE 1

Preparation of 5,7-dimethyl-2-mercapto-1,2,4-triazolo[1,5-a]pyrimidine

A solution of 10.1 g (0.0870 mol) of 3-amino-5-mercapto-1,2,4 triazole, 8.71 g (0.0870 mol) of 2,4-pentanedione and 0.8 ml of piperidine in 300 ml of HOAc was heated at reflux for 21.5 hours. After cooling to room temperature, the solid which separated was collected by filtration and dried in vacuo to yield 13.4 g of pale yellow needles, m.p. 245°–246° C. (decomposition); ^1H NMR (DMSO-d_6-$CDCl_3$) δ13.9 (1H, broad, SH), 7.19 (1H, broad s, H in 6-position) 2.63 and 2.51 (3H each, s, CH_3 groups in 5- and 7-positions), IR (KBr) ~2680, 1628, 1560, 1400 and 1170 cm^{-1}. An analytical sample was prepared by recrystallization from acetic acid to yield colorless plates, m.p. 243.5°–244.5° C. (decomposition).

Analysis:

Calculated for $C_7H_8N_4S$: C, 46.65, H, 4.47; N, 31.09;

Found: C, 46.34; H, 4.41; N, 30.82;

EXAMPLE 2

Preparation of 2-benzylthio-5,7-dimethyl-1,2,4-triazolo[1,5-a]pyrimidine

Twenty percent NaOH (14.0 g, 70 mmol) was added dropwise to a suspension of 11.5 g (64.0 mmol) of the mercaptan prepared in Example 1 in 125 ml of H_2O over about 5 minutes. Benzyl chloride (7.4 ml, 8.1 g, 64 mmol) in 20 ml of CH_3OH was added and the resulting mixture was vigorusly stirred at room temperature for 24 hours. The solid which began separating shortly after the addition of benzyl chloride was collected by filtration and dried in vacuo to afford 16.1 g of white solid, m.p. 134°-135° C. (lit m.p. 132°-134° C., T. Novinson et al, *J. Med. Chem.*, 25, 420 (1982)): ^1H NMR ($CDCl_3$) δ 7.1-7.6 (5H, m, Ph), 6.63 (1H, s, H in 6-position), 4.50 (2H, s, —CH_2S—), 2.67 and 2.58 (3H each, s, CH_3 groups in 5- and 7-positions); IR ($CHCl_3$) 1620, 1447, 1339 and 1295 cm^{-1}. 93% yield.

Analysis:

Calculated for $C_{14}H_{14}N_4S$: C, 62.20; H, 5.22; N, 20.72.
Found: C, 62.21; H, 5.14; N, 20.89.

EXAMPLE 3

Preparation of 2-benzylthio-6,7-cyclopentano-5-methyl-1,2,4-triazolo[1,5-a]pyrimidine

A solution of 51.6 g (0.250 mol) of 3-amino-5-benzylthio-1,2,4-triazole and 31.5 g (0.250 mol) of 2-acetylcyclopentanone in 600 ml of HOAc was heated at reflux for 9.5 hours. The solvent was removed by evaporation, and the brown solid residue was recrystallized from EtOH to yield a light brown solid. A second recrystallization from EtOH gave 45.4 g (61 percent) of the desired product as a light brown solid, m.p. 157°-158.5° C.: ^1H NMR ($CDCl_3$) δ7.0-7.6 (5H, m), 4.51 (2H, s), 3.29 (2H, t), 2.97 (2H, t), 2.0-2.7 (5H, m including s at 2.52); IR ($CHCl_3$) 1621, 1343 and 1290 cm^{-1}.

Analysis:

Calculated for $C_{16}H_{16}N_4S$: C, 64.84; H, 5.44, N, 18.90; S, 10.82.
Found: C, 64.88; H, 5.47; N, 18.98; S, 10.72.

EXAMPLE 4

Preparation of 2-benzylthio-5,6,7-trimethyl-1,2,4-triazolo[1,5-a]pyrimidine

A solution of 51.6 g (0.250 mol) of 3-amino-5-benzylthio-1,2,4-triazole and 28.5 g (0.250 mol) of 3-methyl-2,4-pentanedione in 350 ml of glacial acetic acid was heated at reflux for 17 hours. Upo cooling to room temperature, the reaction mixture was poured onto ice. The pale yellow solid which separated was collected by filtration, washed with water and dried in vacuo to yield 67.1 g (94%) of the desired product as a pale yellow solid, m.p. 133.5°-135° C. The IR and ^1H NMR spectra were consistent with the assigned structure.

Analysis:

Calculated for $C_{15}H_{15}N_4S$: C, 63.35; H, 5.67; N, 19.70; S, 11.27.
Found: C, 63.07; H, 5.48; N, 19.71; S, 11.09.

EXAMPLE 5

Preparation of 2-benzylthio-6-chloro-1,2,4-triazolo[1,5-a]pyrimidine

A solution of 6.52 g (31.6 mmol) of 3-amino-5-benzylthio-1,2,4-triazole and 9.09 g (31.6 mmol) of 1,3-bis(-dimethylamino)-2-chlorotrimethinium perchlorate in 100 ml of glacial acetic acid was heated at reflux for 19 hours. After cooling to room temperature, the solution was poured into 300 ml of water. The solid which separated was collected by filtration, washed with water and dried in vacuo to yield 4.12 g (48%) of the desired product as a brown solid, m.p. 119.5°-135° C. (decomposition). IR and ^1H NMR spectra were consistent with the assigned structure.

Analysis:

Calculated for $C_{12}H_9ClN_4S$: C, 51.90; H, 3.20; N, 20.24.
Found: C, 51.87; H, 3.42; N, 19.81.

EXAMPLE 6

Preparation of 2-benzylthio-1,2,4-triazolo-[1,5-a]pyrimidine

A solution of 2.0 g (9.6 mmol) of 3-amino-5-benzylthio-1,2,4-triazole and 2.3 ml (9.6 mmol) of malonaldehyde bis(diethylacetal) in 20 ml of glacial acetic acid was heated at reflux for 17 hours. After cooling to room temperature, the solvent was removed by evaporation at reduced pressure. The brown solid residue was recrystallized from isopropyl alcohol to afford 0.4 g (17%) of the desired product as a light brown crystalline solid, m.p. 104°-106° C. IR and ^1H NMR spectra were consistent with the assigned structure.

Analysis:

Calculated for $C_{12}H_{10}N_4S$: C, 59.52; H, 4.13; N, 23.13.
Found: C, 59.19; H, 4.09; N, 22.73.

EXAMPLE 7

Preparation of 2-benzylthio-5-methyl-1,2,4-triazolo[1,5-a]pyrimidine

A solution of sodium ethoxide in EtOH was prepared by dissolving 0.54 g (24 mg-atoms) of sodium metal in 120 ml of anhydrous EtOH, and 10.0 g (48 mmol) of 3-amino-5-benzylthio-1,2,4-triazole was added. After stirring for 15 minutes at room temperature, 6.4 ml (6.35 g, 48.4 mmol) of acetylacetaldehyde dimethyl acetal dissolved in 100 ml of absolute EtOH was was added dropwise. After the addition was complete the reaction mixture was stirred at room temperature for 68 hours. The product which separated from solution was collected by filtration and dried to give 10.1 g (83%) of tan solid, m.p. 128.5°-130° C. IR and ^1H NMR spectra were in agreement with the assigned structure.

Analysis:

Calculated for $C_{13}H_{12}N_4S$: C, 60.94; H, 4.68; N, 21.86.
Found: C, 60.69; H, 4.61; N, 21.85.

EXAMPLE 8

Preparation of 2-benzylthio-5-hydroxy-7-methyl-1,2,4-triazolo[1,5-a]pyrimidine

Ethyl 2,3-dibromobutyrate (1.33 g, 48.5 mmol) was added dropwise over 15 minutes to a solution of 10 g (49 mmol) of 3-amino-5-benzylthio-1,2,4-triazole in 20 ml of pyridine heated to 65° C. After the addition was complete, the reaction mixture was heated at 65° C. for 20 hours, cooled to room temperature and filtered. The filtrate was concentrated by evaporation at reduced pressure. The residue was triturated with methanol to separate 1.64 g (13%) of the desired product as a colorless crystalline solid, m.p. 219°-220° C. IR and ^1H NMR spectra were in agreement with the assigned structure.

Analysis:

Calculated for $C_{13}H_{12}N_4OS$: C, 57.37; H, 4.41; N, 20.60.

Found: C, 56.86; H, 4.41; N, 20.72.

EXAMPLE 9

Preparation of 2-benzylthio-5-methoxy-7-methyl-1,2,4-triazolo[1,5-a]pyrimidine

A solution of 2.67 g (9.80 mmol) of 2-benzylthio-5-hydroxy-7-methyl-1,2,4-triazolo[1,5-a]pyrimidine in 50 ml of phosphorous oxychloride was heated at reflux for 3 hours. The excess phosphorous oxychloride was removed by evaporation at reduced pressure. The residue was partitioned between CH_2Cl_2 and cold water. The organic phase was separated, dried ($MgSO_4$) and concentrated by evaporation at reduced pressure. The resulting solid was added to 50 ml (0.22 mol) of a 25 weight percent solution of sodium methoxide in methanol. The resulting suspension was stirred at room temperature for 30 minutes, diluted with 50 ml of water and filtered. The solid collected was dried in vacuo to yield 1.41 g (41%) of the desired product as a light brown solid, m.p. 112.5°-115° C. IR and ^1H NMR spectra were consistent with the assigned structure.

EXAMPLE 10

Preparation of 2-benzylthio-7-methyl-1,2,4-triazolo[1,5-a]pyrimidine

A solution of 50 g (0.24 mol) of 3-amino-5-benzylthio-1,2,4-triazole in 500 ml of glacial acetic acid was added dropwise over 3-4 hours to a solution of 34.0 g (0.25 mol) of acetylacetaldehyde dimethyl acetal in 500 ml of glacial acetic acid heated at 100° C. After the addition was complete the reaction mixture was heated at reflux overnight, cooled to room temperature and poured into an ice-water mixture. The solid which separated was collected by filtration and recrystallized from ethanol to yield 27 g (41%) of the desired product as a solid, m.p. 102°-104° C. IR and ^1H NMR spectra were in agreement with the assigned structure.

Analysis:

Calculated for $C_{13}H_{12}N_4S$: C, 60.94; H, 4.68; N, 21.85.

Found: C, 60.81; H, 4.68; N, 21.74.

EXAMPLE 11

Preparation of 2-benzylthio-6-methyl-1,2,4-triazolo[1,5-a]pyrimidine

A suspension of 14.4 g (0.124 mol) of 3-amino-5-benzyl-1,2,4-triazole and 30.0 g (0.124 mol) of 1,3-bis(dimethylamino)-2-methyltrimethinium perchlorate in 500 ml of glacial acetic acid was heated at reflux for 63 hours. The reaction mixture was subjected to the work-up described in Example 5 to yield 13.9 g (68%) of the desired product as a brown solid, m.p. 254°-256° C. IR and ^1H NMR spectra were in agreement with the assigned structure.

Analysis:

Calculated for $C_6H_6N_4S$: C, 43.35; H, 3.61; N, 33.72

Found: C, 42.71; H, 3.49; N, 33.26.

EXAMPLE 12

Preparation of 2-benzylthio-6-chloro-5,7-dimethyl-1,2,4-triazolo[1,5-a]pyrimidine

To a suspension of 153 g (0.74 mol) 3-amino-5-benzylthio-1,2,4-triazole in 250 ml of glacial acetic acid was added 100 g (0.74 mol) of 3-chloro-2,4-pentanedione in a dropwise manner. The reaction mixture was heated at reflux for 18 hours and cooled to room temperature. The reaction mixture was poured over ice and the oil which separated solidified upon stirring. The solid was collected by filtration and recrystallized from methanol to yield 116 g (79%) of the desired product as an off white solid, m.p. 164°-166° C. IR and ^1H NMR spectra were in agreement with the assigned structure.

Analysis:

Calculated for $C_{14}H_{13}ClN_4S$: C, 55.16; H, 4.30; N, 18.38.

Found: C, 55.11; H, 4.30; N, 18.34.

EXAMPLE 13

Preparation of 2-benzylthio-6-ethoxy-1,2,4-triazolo[1,5-a]pyrimidine

This material was prepared in 28% yield from 3-amino-5-benzylthio-1,2,4-triazole and 1,3-bis(dimethylamino)-2-ethoxytrimethinium perchlorate following the general procedure described in Example 5. The desired product was isolated as a solid, m.p. 139°-140° C. IR and ^1H NMR spectra were in agreement with the assigned structure.

Analysis:

Calculated for $C_{14}H_{14}N_4OS$: C, 58.73; H, 4.89; N, 19.57.

Found: C, 58.68; H, 4.64; N, 19.58.

EXAMPLE 14

Preparation of 2-benzylthio-2-benzylthio-5-isopropyl-1,2,4-triazolo[1,5-a]pyrimidine

This material was prepared in 96% yield from 3-amino-5-benzylthio-1,2,4-triazole and 4-methyl-3-oxopentanal following the general procedure described in Example 7. The desired product was isolated as a solid, m.p. 65°-66° C. IR and ^1H NMR were in agreement with the assigned structure.

Analysis:

Calculated for $C_{15}H_{16}N_4S$: C, 63.36; H, 5.63; N, 19.71.

Found: C, 63.00; H, 5.62; N, 19.62.

EXAMPLE 15

Preparation of 2-benzylthio-5,6-dimethyl-1,2,4-triazolo[1,5-a]pyrimidine

A solution of 5.0 g (24 mmol) of 3-amino-5-benzylthio-1,2,4-triazole and 5.0 g (41 mmol) of the sodium salt of 2-methyl-3-oxobutanal in 200 ml of glacial acetic acid was heated at reflux overnight. The solution was cooled to room temperature and the reaction mixture was concentrated by evaporation at reduced pressure. The residue was combined with ice and H_2O to separate a tan solid. The solid was collected by filtration, dried and carefully recrystallized from ethyl acetate to yield 3.53 g (54%) of the desired product as a crystalline solid, m.p. 147°-149° C. IR and ^1H NMR spectra were in agreement with the assigned structure.

Analysis:

Calculated for $C_{14}H_{14}N_4S$: C, 62.10; H, 5.18; N, 20.72.
Found: C, 61.58; H, 5.18; N, 20.45.

EXAMPLE 16

Preparation of 2-benzylthio-6-chloro-7-hydroxy-5-methyl-1,2,4-triazolo[1,5-a]pyrimidine

A solution of 16 g (77 mmol) of 3-amino-5-benzylthio-1,2,4-triazole and 10.6 g (77 mmol) of ethyl 2-chloroacetoacetate in 150 ml of glacial acetic acid was heated at 100° C. for 17 hours. Upon cooling to room temperature the solid which separated was collected by filtration. The filtrate was diluted with ice water to separate an additional quantity of solid. The solids were combined and dried to yield 14.0 g (60% of the desired product as a solid, m.p. 258°-260° C. IR and ^1H NMR were in agreement with the assigned structure.

Analysis:

Calculated for $C_{13}H_{11}ClN_4OS$: C, 50.89; H, 3.58; N, 18.27.

Found: C, 50.51; H, 3.36; N, 18.67.

EXAMPLE 17

Preparation of 2-benzylthio-6,7-dichloro-5-methyl-1,2,4-triazolo[1,5-a]pyrimidine

This material was prepared in 68% yield from 2-benzylthio-6-chloro-7-hydroxy-5-methyl-1,2,4-triazolo[1,5-a]pyrimidine and phosphorus oxychloride following the general procedure described in Example 20. The desired product was isolated as a solid, m.p. 103°-105° C. IR and ^1H NMR spectra were in agreement with the assigned structure.

Analysis:

Calculated for $C_{13}H_{10}Cl_2N_4S$: C, 48.00; H, 3.07; N, 17.23.

Found: C, 47.40; H, 3.00; N, 17.43.

EXAMPLE 18

Preparation of 2-benzylthio-6-chloro-5-methyl-1,2,4-triazolo[1,5-a]pyrimidine

This material was prepared by reduction of 2-benzylthio-6,7-dichloro-5-methyl-1,2,4-triazolo[1,5-a]pyrimidine with zinc-copper couple following the general procedure described in Example 21. The desired product was isolated in 88% yield as a solid, m.p. 160°-161° C. IR and ^1H NMR spectra were in agreement with the assigned structure.

Analysis:

Calculated for $C_{13}H_{11}ClN_4S$: C, 53.56; H, 3.56; N, 19.27.

Found: C, 53.30; H, 3.79; N, 19.28.

EXAMPLE 19

Preparation of 2-benzylthio-5,7-dihydroxy-1,2,4-triazolo[1,5-a]pyrimidine

A solution of 125 g (0.58 mol) of a 25% solution of sodium methoxide in methanol dissolved in 100 ml of absolute ethanol was treated with 66.3 ml (0.29 mol) of dimethyl malonate followed by 60.0 g (0.20 mol) of 3-amino-5-benzylthio-1,2,4-triazole. The resulting solution was heated at reflux for 5 days. On cooling to room temperature the solid which had separated was collected by filtration, washed with cold ethanol and dissolved in 1000 ml of water. The resulting yellow solution was acidified with concentrated HCl to precipitate a solid. The solid was collected by filtration and dried to yield 70.1 g (82%) of the desired product as a white solid, m.p. 199°-210° C. (decomposition). IR and ^1H NMR spectra were in agreement with the assigned structure.

Analysis:

Calculated for $C_{12}H_{10}N_4O_2S.H_2O$: C, 49.30; H, 4.14, N, 19.16.

Found: C, 48.70; H, 3.89; N, 18.83.

EXAMPLE 20

Preparation of 2-benzylthio-5,7-dichloro-1,2,4-triazolo[1,5-a]pyrimidine

A suspension of 70.0 g (0.24 mol) of 2-benzylthio-5,7-dihydroxy-1,2,4-triazolo[1,5-a]pyrimidine and 67.0 ml (0.72 mol) of phosphorous oxychloride in 600 ml of acetonitrile was heated at reflux for 3 hours. The resulting orange solution was stirred at room temperature overnight (17 hours). The solution was filtered and the filtrate was concentrated by evaportion at reduced pressure. The residue was partitioned between cold water and methylene chloride, and the organic phase was separated and dried ($MgSO_4$). The organic phase was concentrated to induce crystallization. The desired product was collected by filtration to yield 98.0 g (81%) of solid, m.p. 97°-100° C. IR and ^1H NMR spectra were in agreement with the assigned structure.

Analysis:

Calculated for $C_{12}H_8Cl_2N_4S$: C, 46.32; H, 2.59; N, 18.00.

Found: C, 46.43; H, 2.57; N, 18.08.

EXAMPLE 21

Preparation of 2-benzylthio-5-chloro-1,2,4-triazolo[1,5-a]pyrimidine

A zinc-copper couple was prepared following the precedure of Bradley (*J. Org. Chem.* 31, 626 (1966)) by stirring 1.0 g of copper sulfate in 20 ml of water with 15.0 g of zinc dust for 2 hours. The couple was collected by filtration, washed with acetone and dried overnight under vacuum at 100° C. To a solution of 33.0 g (106 mmol) of 2-benzylthio-5,7-dichloro-1,2,4-triazolo[1,5-a]pyrimidine in 12.5 ml (213 mmol) of acetic acid, 50 ml of methanol and 300 ml of tetrahydrofuran was added 20.5 g of Zn-Cu couple. The mixture was stirred overnight at 22°-23° C. When the reaction was complete (TLC analysis) the reaction mixture was filtered through celite and the filtrate was concentrated by evaporation at reduced pressure. The residue was triturated with hexane to separate a solid. The solid was collected by filtration to yield the desired product as 26.5 g (92%) of orange solid, m.p. 125°-127° C. IR and ^1H NMR spectra were in agreement with the assigned structure.

Analysis:

Calculated for $C_{12}H_9ClN_4S$: C, 52.08; H, 3.25; N, 20.25.
Found: C, 51.76; H, 3.00; N, 20.27.

EXAMPLE 22

Preparation of 2-benzylthio-5-methoxy-1,2,4-triazolo[1,5-a]pyrimidine

A mixture of 6.0 g (22 mmol) of 2-benzylthio-5-chloro-1,2,4-triazolo[1,5-a]pyrimidine in 25 ml of methanol was treated with 5.0 g (23.8 mmol) of a 25% solution of sodium methoxide in methanol. After stirring for 1.5 hours the reaction mixture was diluted with 100 ml of water and neutralized with 3N HCL (aq). The solid which separated was collected by filtration, washed with water and dried to afford 5.0 g (84%) of the desired product as a white solid, m.p. 126°-128° C. IR and [1]H NMR spectra were in agreement with the assigned structure.

Analysis:

Calculated for $C_{13}H_{12}N_4OS$: C, 57.34; H, 4.41; N, 20.58.

Found: C, 57.21; H, 4.42; N, 20.13.

EXAMPLE 23

Preparation of 2-benzylthio-5-(2,2,2-trifluoroethoxy)-1,2,4-triazolo[1,5-a]pyrimidine

A solution of sodium 2,2,2-trifluoroethoxide in tetrahydrofuran was prepared by the addition of 1.1 g (48 mg-atom) of sodium metal to a solution of 3.5 ml (48 mmol) of 2,2,2-trifluoroethanol in 100 ml of tetrahydrofuran. To this solution was added 7.0 g (25 mmol) of 2-benzylthio-5-chloro-1,2,4-triazolo[1,5-a]pyrimidine, and the reaction mixture was stirred for 30 minutes and concentrated by evaporation at reduced pressure to approximately one quarter of the original volume. Pentane (200 ml) was added to induce crystallization. The solid which separated was collected by filtration to yield 6.42 g (75%) of the desired product as a light yellow solid, m.p. 114°-118° C. IR and [1]H NMR spectra were in agreement with the assigned structure.

Analysis:

Calculated for $C_{14}H_{11}F_3N_4OS$: C, 49.40; H, 3.23; N, 16.46.

Found: C, 49.63; H, 3.09; N, 16.70.

EXAMPLE 24

Preparation of 2-benzylthio-5-ethoxy-1,2,4-triazolo[1,5-a]pyrimidine

This material was prepared by heating 2 benzylthio-5-(2,2,2-trifluoroethoxy)-1,2,4-triazolo[1,5-a]pyrimidine in boiling ethanol. The hot mixture was filtered and the filtrate was concentrated. The crude product was recrystallized from isopropanol to yield the desired product as a solid, m.p. 115°-117° C. IR and [1]H NMR spectra were in agreement with the assigned structure.

Analysis:

Calculated for $C_{14}H_{14}N_4OS$: C, 58.73; H, 4.89; N, 19.31; S, 11.20.

Found: C, 57.90; H, 4.69; N, 19.30; S, 10.79.

EXAMPLE 25

Preparation of 2-benzylthio-5,7-dihydroxy-6-methyl-1,2,4-triazolo[1,5-a]pyrimidine

This material was prepared in 80% yield from 3-amino-5-benzylthio-1,2,4-triazole and dimethyl 2-methyl malonate following the general procedure described in Example 19. The product was isolated as a solid, m.p. 260°-272° C. (decomposition). IR and [1]H NMR spectra were in agreement with the assigned structure.

Analysis:

Calculated for $C_{13}H_{12}N_4O_2S$: C, 54.15; H, 4.16; N, 19.44.

Found: C, 53.48; H, 4.07; N, 19.53.

EXAMPLE 26

Preparation of 2-benzylthio-5,7-dichloro-6-methyl-1,2,4-triazolo[1,5-a]pyrimidine

This material was prepared in 97% yield from the reaction of 2-benzylthio-5,7-dihydroxy-6-methyl-1,2,4-triazolo[1,5-a]pyrimidine and phosphorous oxychloride following the general procedure described in Example 20. The product was isolated as a solid, m.p. 121°-123° C. IR and [1]H NMR spectra were in agreement with the assigned structure.

Analysis:

Calculated for $C_{13}H_{10}Cl_2N_4S$: C, 48.01; H, 3.08; N, 17.23.

Found: C, 47.65; H, 3.11; N, 17.70.

EXAMPLE 27

Preparation of 2-benzylthio-5-chloro-6-methyl-1,2,4-triazolo[1,5-a]pyrimidine

This material was prepared in 32% yield by reduction of 2-benzylthio-5,7-dichloro-6-methyl-1,2,4-trizolo[1,5-a]pyrimidine with zinc-copper couple following the general procedure described in Example 21. The desired product was isolated as a solid, m.p. 179°-181° C. IR and [1]H NMR spectra were in agreement with the assigned structure.

Analysis:

Calculated for $C_{13}H_{11}ClN_4S$: C, 53.70; H, 3.79; N, 19.28.

Found: C, 53.33; H, 3.73; N, 19.53.

EXAMPLE 28

Preparation of 2-benzylthio-5-methoxy-6-methyl-1,2,4-triazolo[1,5-a]pyrimidine

This material was prepared in 64% yield by reaction of 2-benzylthio-5-chloro-6-methyl-1,2,4-triazolo[1,5-a]pyrimidine with sodium methoxide following the general procedure described in Example 22. The desired product was isolated as a solid, m.p. 145°-146° C. IR and [1]H NMR spectra were in agreement with the assigned structure.

Analysis:

Calculated for $C_{14}H_{14}N_4OS$: C, 58.73; H, 4.89; N, 19.58.

Found: C, 58.34; H, 4.84; N, 19.67.

EXAMPLE 29

Preparation of 2-benzylthio-6-ethoxycarbonyl-7-methyl-1,2,4-triazolo[1,5-a]pyrimidine

A solution of 15 g (73 mmol) of 3-amino-5-benzylthio-1,2,4-triazole and 15.0 g (80.0 mmol) of ethyl ethoxymethyleneacetoacetate in 250 ml of glacial acetic acid was heated at reflux for 60 hours. After cooling the volume of the reaction was reduced to approximately one quarter of the original volume by evaporation at reduced pressure. The resulting residue was poured into water, and the solid which separated was collected by filtration, washed with water and dried to yield 7.88 g (33%) of the desired product as a solid, m.p. 98°-99° C. IR and [1]H NMR spectra were in agreement with the assigned structure.

Analysis:

Calculated for $C_{16}H_{16}N_4O_2S$: C, 58.52; H, 4.87; N, 17.07.

Found: C, 58.51; H, 4.89; N, 17.03.

EXAMPLE 30

Preparation of 2-benzylthio-6-(4-nitrophenyl)-1,2,4-triazolo[1,5-a]pyrimidine

This material was prepared from 3-amino-5-benzylthio-1,2,4-triazole and 1,3-bis(dimethylamino)-2-(4-nitrophenyl)-trimethinium percholate following the general procedure described in Example 5. The desired product was isolated as a solid, m.p. 195°-199° C. IR and ^1H NMR spectra were in agreement with the assigned structure.

EXAMPLE 31

Preparation of 2-benzylthio-5,6-cyclopentano-7-hydroxy-1,2,4-triazolo[1,5-a]pyrimidine

A solution of 20.6 g (100 mmol) of 3-amino-5-benzylthio-1,2,4-triazole and 15 ml (16 g, 0.10 mol) of 2-carboethoxycyclopentanone in 110 ml of glacial acetic acid was heated at reflux for 23 hours. After cooling to room temperature the solid which separated from the reaction mixture was collected by filtration, washed with acetic acid and dried in vacuo to yield 22.4 g (75%) of the desired product as a colorless crystalline solid, m.p. 241°-243° C. IR and ^1H NMR spectra were in agreement with the assigned structure.

Analysis:

Calculated for $C_{15}H_{14}N_4OS$: C, 60.38; H, 4.73; N, 18.78; S, 10.75.

Found: C, 60.10; H, 4.66; N, 18.91; S, 10.72.

EXAMPLE 32

Preparation of 2-benzylthio-7-chloro-5,6-cyclopentano-1,2,4-triazolo[1,5-a]pyrimidine

A solution of 5.97 g (20.0 mmol) of 2-benzylthio-5,6-cyclopentano-7-hydroxy-1,2,4-triazolo[1,5-a]pyrimidine in 250 ml of phosphorus oxychloride was heated at reflux for 50 minutes. After cooling to room temperature the excess phosphorous oxychloride was removed by distillation at aspirator pressure. The residue was partitioned between ice cold water and methylene chloride. The organic phase was dried (Na_2SO_4) and evaporated at reduced pressure. The residue was chromatographed on silica gel eluting with EtOAc hexane (1:1, v/v) to yield 3.72 g (59%) of the desired product as a yellow solid, m.p. 119°-120° C. IR and ^1H NMR spectra were in agreement with the assigned structure.

Analysis:

Calculated for $C_{15}H_{13}ClN_4S$: C, 56.87; H, 4.14; N, 17.68; Cl, 11.19; S, 10.12.

Found: C, 56.91; H, 4.06; N, 17.83; Cl, 10.68; S; 9.65.

EXAMPLE 33

Preparation of 2-benzylthio-5,6-cyclopentano-7-methyl-1,2,4-triazolo[1,5-a]pyrimidine

A solution of 2.47 g (7.80 mmol) of 2-benzylthio-7-chloro-5,6-cyclopentano-1,2,4-triazolo[1,5-a]pyrimidine in 40 ml of dry tetrahydrofuran was cooled to 5° C. and 5.9 ml (17 mmol) of 2.9M methyl magnesium bromide in ether was added over 5 minutes. After the addition was complete the reaction mixture was warmed to room temperature and stirred overnight (17 hours). The reaction was quenched by addition of 10 ml of saturated aqueous ammonium chloride. The organic phase was separated, dried (Na_2SO_4) and evaporated at reduced pressure. The red oil residue was chromatographed on silica gel (HPLC) eluting with EtOAc-hexane (1:1, v/v) to yield 1.12 g (48%) of the desired product as a pale red solid, m.p. 109°-111° C. IR and ^1H NMR spectra were in agreement with the assigned structure.

Analysis:

Calculated for $C_{16}H_{16}N_4S$: C, 64.84; H, 5.44; N, 18.90; S, 10.82.

Found: C, 64.99; H, 5.41; N, 18.16; S, 10.42.

EXAMPLE 34

Preparation of 2-benzylthio-5,7-bis-(trifluoromethyl)-1,2,4-triazolo[1,5-a]pyrimidine

A solution of 20.8 g (0.100 mol) of 1,1,1,5,5,5-hexafluoro-2,4-pentanedione and 20.6 g (0.100 mol) of 3-amino-5-benzylthio-1,2,4-triazole in 150 ml of glacial acetic acid was heated at reflux for 14 hours. The solution was cooled to room temperature and poured over ice. The solid which separated was collected by filtration, washed with water and dried in vacuo to yield 35.5 g (94%) of the desired product as a pale yellow solid, m.p. 78.5°-80.5° C. IR, ^1H NMR and ^{19}F NMR spectra were in agreement with the assigned structure.

Analysis:

Calculated for $C_{14}H_8F_6N_4S$: C, 44.45; H, 2.13; N, 14.81; S, 8.48.

Found: C, 44.53; H, 2.15; N, 14.97; S, 8.39.

EXAMPLE 35

Preparation of 2-benzylthio-5-methyl-7-trifluoromethyl-1,2,4-triazolo[1,5-a]pyrimidine

This material was prepared in 84% yield from 3-amino-5-benzylthio-1,2,4-triazole and 1,1,1-trifluoro-2,4-pentanedione following the general procedure described in Example 34. The product was purified by recrystallization from benzene-hexane to yield a tan solid, m.p. 83.5°-84.5° C. IR, ^1H NMR and ^{19}F NMR spectra were in agreement with the assigned structure.

Analysis:

Calculated for $C_{14}H_{11}F_3N_4S$: C, 51.85; H, 3.42; N, 17.27; S, 9.89.

Found: C, 51.73; H, 3.44; N, 18.01; S, 10.08.

EXAMPLE 36

Preparation of 2-benzylthio-5,7-diphenyl-1,2,4-triazolo[1,5-a]pyrimidine

A solution of 8.40 g (37.5 mmol) of dibenzoylmethane and 7.73 g (37.5 mmol) of 3-amino-5-benzylthio-1,2,4-triazole in 50 ml of glacial acetic acid was heated at reflux for 24 hours. Upon cooling to room temperature the solid which separated was collected by filtration and dried. The product was chromatographed on silica gel (HPLC) eluting with EtOAc-hexane (3:7, v/v) to afford 5.08 g (34%) of the desired product as a colorless solid, m.p. 122.5°-123.5° C. IR and ^1H NMR spectra were in agreement with the assigned structure.

Analysis:

Calculated for $C_{24}H_{18}N_4S$: C, 73.07; H, 4.60; N, 14.20; S, 8.13.

Found: C, 73.48; H, 4.54; N, 14.17; S, 7.97.

EXAMPLE 37

Preparation of 2-benzylthio-5-methyl-7-phenyl-1,2,4-triazolo[1,5-a]pyrimidine and 2-benzylthio-7-methyl-5-phenyl-1,2,4-triazolo[1,5-a]pyrimidine

A solution of 20.6 g (100 mmol) of 3-amino-5-benzylthio-1,2,4-triazole and 16.2 g (100 mmol) of benzoyl acetone in 100 ml of glacial acetic acid was heated at reflux for 14 hours. The solvent was removed by evaporation at reduced pressure and the residue was chromatographed on silica gel (HPLC) eluting with EtOAc-hexane (3:7, v/v) to afford 4.81 g (14% of 2-benzylthio-7-methyl-5-phenyl-1,2,4-triazolo[1,5-a]pyrimidine as a pale yellow wolid, m.p. 154°-155° C. IR and ^{1}H NMR spectra were in agreement with the assigned structure.

Analysis:

Calculated for $C_{19}H_{16}N_4S$: C, 68.65; H, 4.85; N, 16.85; S, 9.65.

Found: C, 68.76; H, 4.82; N, 16.98; S, 9.93.

Further elution afforded 22.8 g (69%) of 2-benzylthio-5-methyl-7-phenyl-1,2,4-triazolo[1,5-a]pyrimidine as a pale yellow solid, m.p. 110°-111° C. IR and ^{1}H NMR spectra were in agreement with the assigned structure.

Analysis:

Calculated for $C_{19}H_{16}N_4S$: C, 68.65; H, 4.85; N, 16.85; S, 9.65.

Found: C, 68.52; H, 4.75; N, 16.93; S, 9.61.

EXAMPLE 38

Preparation of 5,7-dimethyl-1,2,4-triazolo[1,5-a]pyrimidine-2-sulfonyl chloride

Chlorine was bubbled into a suspension of 99.0 g (0.366 mol) of 2-benzylthio-5,7-dimethyl-1,2,4-triazolo[1,5-a]pyrimidine in 700 ml of HOAc-H_2O (1:1, v/v) cooled to −1° C. During the course of the addition the temperature of the reaction mixture was maintained below 5° C. After 2.5 hours the chlorine addition was ceased and the reaction mixture was filtered to collect a tan solid. The filtrate was diluted with H_2O to separate an additional quantity of solid which was collected by filtration. The combined solid products were dried in vacuo to yield 70.4 g (78%) of crude sulfonyl chloride III (X=Z=Me, Y=H) as a tan solid. IR and ^{1}HNMR spectra confirmed the structure.

Recrystallization from EtOAc produced an analytical sample as an off-white solid, m.p. 128.5°-130.5° C.

Analysis:

Calculated for $C_7H_7ClN_4O_2S$: C, 34.09; H, 2.86; N, 20.73; S, 13.00.

Found: C, 34.34; H, 2.80; N, 22.64; S, 12.85.

EXAMPLE 39

Preparation of 6,7-cyclopentano-5-methyl-1,2,4-triazolo[1,5-a]pyrimidine-2-sulfonyl chloride

Chlorine gas was bubbled into a suspension of 4.45 g (15.0 mmol) of 2-benzylthio-6,7-cyclopentano-5-methyl-1,2,4-triazolo[1,5-a]pyrimidine in 30 ml of HOAC-H_2O (1:1, v/v) cooled to −4° C. After 30 minutes the addition was stopped and the reaction was stirred for 30 minutes maintaining the temperture below 5° C. The reaction mixture was filtered and the collected solid was dried under vacuum to yield 3.46 g (85 percent) of the desired sulfonyl chloride as a cream colored solid which was used directly without further purification: IR ($CHCl_3$) 1627, 1551, 1398 and 1170 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ3.50 (2H, broad t), 3.18 (2H, broad t) and 2.2-2.8 (5H, broad t), 3.18 (2H, broad t) and 2.2-2.8 (5H, m including s at 2.68).

EXAMPLE 40

Preparation of 5,6,7-trimethyl-1,2,4-triazolo[1,5a]pyrimidine-2-sulfonyl chloride

Chlorine was bubbled into a suspension of 28.4 g (0.100 mol) of 2-benzylthio-5,6,7-trimethyl-1,2,4-triazolo[1,5-a]pyrimidine in 200 ml of glacial acetic acid-H_2O (1:1, v/v) and cooled to −5° C. The chlorine addition continued over 35 minutes and the temperature of the reaction mixture never exceeded 5° C. After the addition was complete, the reaction mixture was stirred for 5 minutes and filtered. The solid collected was washed twice with H_2O and dried in vacuo to yield 24.3 g (93%) of the crude sulfonyl chloride as a pale yellow solid. The IR and ^{1}H NMR were consistent with the assigned structure. The crude solfonyl chloride was used in subsequent transformations without further purification.

EXAMPLE 41

Preparation of 6-chloro-1,2,4-triazolo[1,5-a]pyrimidine-2-sulfonyl chloride

A suspension of 3.75 g (13.5 mmol) of 2-benzylthio-6-chloro-1,2,4-triazolo[1,5-a]pyrimidine in 40 ml of AcOH-H_2O (1:1, v/v) was cooled to −10° C. and chlorine gas was bubbled into the reaction mixture for 10 minutes. After the addition was complete, the reaction mixture was stirred for 10 minutes and diluted with 25 ml of H_2O. The mixture was filtered and the filtrate was extracted with CH_2Cl_2. The organic phase was evaporated at reduced pressure to afford 2.14 g of the crude sulfonyl chloride as a liquid. IR and ^{1}H NMR spectra were in agreement with the assigned structure.

EXAMPLE 42

Preparation of 1,2,4-triazolo[1,5-a]-pyrimidine-2-sulfonyl chloride

A suspension of 8.0 g (33 mmol) of 2-benzylthio-1,2,4-triazolo[1,5-a]pyrimidine in 60 ml of HOAc-H_2O (1:1, v/v) was cooled below 0° C. and chlorine gas was bubbled into the reaction mixture for 15 minutes. The temperature of the reaction mixture was maintained below 10° C. during the course of the addition. After the addition was complete, the reaction mixture was stirred for 15 minutes, diluted with H_2O and extracted with CH_2Cl_2. The organic phase was dried ($MgSO_4$) and evaporated at reduced pressure to yield 5.74 g of the desired crude product as a brown oil, IR and ^{1}H NMR were in agreement with the assigned structure.

Recrystallization from EtOAc gave an analytical sample, m.p. 105°-109° C.

Analysis:

Calculated for $C_5H_3ClN_4O_2S$: C, 27.45; H, 1.32; N, 25.62.

Found: C, 28.91; H, 1.52; N, 25.79.

EXAMPLE 43

Preparation of 5-methyl-1,2,4-triazolo-[1,5-a]pyrimidine-2-sulfonyl chloride

A suspension of 2.77 g (10.8 mmol) of 2-benzylthio-5-methyl-1,2,4-triazolo[1,5-a]pyrimidine in 40 ml of AcOH-H_2O (1:1, v,v) was cooled to −10° C. and chlorine gas was bubbled into the solution for 10 minutes. After the addition was complete, the reaction mixture was stirred for 5 minutes, diluted with H_2O (25 ml) and filtered. The solid collected was dried in vacuo to yield 1.17 g of the desired sulfonyl chloride. IR and ^1H NMR were in agreement with the assigned structure.

An addition quantity of the product contaminated with by-products containing benzyl residues was obtained byextraction of the filtrate with CH_2Cl_2 and evaporation of the organic phase at reduced pressure.

EXAMPLE 44

Preparation of 5-methoxy-7-methyl-1,2,4-triazolo[1,5-a]pyrimidine-2-sulfonyl chloride

A suspension of 1.41 g (4.93 mmol) of 2-benzylthio-5-methoxy-7-methyl-1,2,4-triazolo[1,5-a]pyrimidine in 40 ml of AcOH-H_2O (1:1, v/v) was cooled to −20° C., and chlorine gas was bubbled into the reaction mixture for 5 minutes. After the addition was complete, the reaction mixture was stirred for 10 minutes, diluted with H_2O (20 ml) and filtered. The solid collected was dried in vacuo to yield 0.63 g of the desired crude sulfonyl chloride as a colorless solid. IR and ^1H NMR were in agreement with the assigned structure.

EXAMPLE 45

Preparation of 7-methyl-1,2,4-triazolo[1,5-a]pyrimidine-2-sulfonyl chloride

A suspension of 3.52 g (13.7 mmol) of 2-benzylthio-5-methyl-1,2,4-triazolo[1,5-a]pyrimidine in 40 ml of AcOH-H_2O (1:1, v/v) was cooled to −10° C., and chlorine gas was bubbled into the reaction mixture for 10 minutes. After the addition was complete, the reaction mixture was stirred for 10 minutes, diluted with H_2O and filtered. The solid collected was dried in vacuo to yield 0.46 g of the desired sulfonyl chloride as a tan solid. IR and ^1H NMR spectra were in agreement with the assigned structure.

An additional quantity (2.2 g) of crude sulfonyl chloride contaminated with by-products containing benzyl residues was obtained by extraction of the filtrate with CH_2Cl_2 and evaporation at reduced pressure.

EXAMPLE 46

Preparation of 6-methyl-1,2,4-triazolo[1,5-a]pyrimidine-2-sulfonyl chloride

A suspension of 10.0 (60 mmol) of 2-benzylthio-6-methyl-1,2,4-triazolo[1,5-a]pyrimidine in 260 ml of methylene chloride, 100 ml of water and 17 ml of concentrated HCl was cooled to −5° C. and treated with 284 ml (197 mmol) of 5.25% aqueous sodium hypochlorite (commercial bleach) by dropwise addition. After the addition was complete the reaction mixture was stirred for 20 minutes at 0° C. and filtered. The organic layer was separated and the aqueous layer was extracted twice with methylene chloride. The combined organic phases were dried ($MgSO_4$) and evaporated at reduced pressure to yield 7.0 g (50%) of the desired product as a solid, mp 106°–108° C. IR and ^1H NMR spectra were in agreement with the assigned structure.

Analysis:

Calculated for $C_6H_5ClN_4O_2S$: C, 30.96; H, 2.15; N, 24.08

Found: C, 31.00; H, 2.23; N, 23.91

EXAMPLE 47

Preparation of 6-chloro-5,7-dimethyl-1,2,4-triazolo[1,5-a]pyrimidine-2-sulfonyl chloride

This material was prepared in 50% yield from 2-benzylthio-6-chloro-5,7-dimethyl-1,2,4-triazolo [1,5-a]pyrimidine following the general procedure described in Examples 38–45. The product was isolated as a pale yellow solid, mp 131°–133° C. IR and ^1H NMR spectra were in agreement with the assigned structure.

EXAMPLE 48

Preparation of 6-ethoxy-1,2,4-triazolo[1,5-a]pyrimidine-2-sulfonyl chloride

This material was prepared in 82% yield from 2-benzylthio-6-ethoxy-1,2,4-triazolo[1,5-a]pyrimidine following the general procedure described in Examples 38–45. The product was isolated as a solid, mp 134°–137° C. IR and ^1H NMR spectra were in agreement with the assigned structure.

Analysis:

Calculated for $C_7H_7ClN_4O_3S$: C, 31.96; H, 2.66; n, 21.31.

Found: C, 32.64; H, 2.36; N, 21.30.

EXAMPLE 49

Preparation of 5-isopropyl-1,2,4-triazolo[1,5-a]pyrimidine-2-sulfonyl chloride

This material was prepared in 56% yield from 2-benzylthio-5-isopropyl-1,2,4-triazolo[1,5-a]pyrimidine following the general procedure described in Example 46. The product was isolated as a solid, mp 60°–62° C. IR and ^1H NMR spectra were in agreement with the assigned structure.

Analysis:

Calculated for $C_8H_9ClN^4O_2S$: C, 36.85; H, 3.45; N, 21.49.

Found: C, 37.02; H, 3.49; N, 21.71.

EXAMPLE 50

Preparation of 5,6-dimethyl-1,2,4-triazolo[1,5-a]pyrimidine-2-sulfonyl chloride

This material was prepared in 80% yield from 2-benzylthio-5,6-dimethyl-1,2,4-triazolo[1,5-a]pyrimidine following the general procedure described in Example 46. The product was isolated as a solid, mp 116°–120° C. IR and ^1H NMR spectra were in agreement with the assigned structure.

Exact mass calculated for $C_7H_7ClN_4O_2S$: 245.9984

Found: 245.9981

EXAMPLE 51

Preparation of 6-chloro-5-methyl-1,2,4-triazolo[1,5-a]pyrimidine-2-sulfonyl chloride

This material was prepared in 60% yield from 2-benzylthio-6-chloro-5-methyl-1,2,4-triazolo[1,5-a]pyrimidine following the general procedure described in Examples 38–45. The product was isolated as a solid, mp 99°–101° C. IR and [1]H NMR spectra were in agreement with the assigned structure.

EXAMPLE 52

Preparation of 5-methoxy-1,2,4-triazolo-[1,5-a]pyrimidine-2-sulfonyl chloride

This material was prepared in 57% yield from 2-benzylthio-5-methoxy-1,2,4-triazolo[1,5-a]pyrimidine following the general procedure described in Examples 38–45. The product was isolated as a solid, mp 110°–112° C. IR and [1]H NMR spectra were in agreement with the assigned structure.

Analysis:

Calculated for $C_6H_5ClN_4O_3S$: C, 28.97; H, 2.01; N, 22.53.

Found: C, 29.90; H, 2.23; N, 22.76.

EXAMPLE 53

Preparation of 5-(2,2,2-trifluoroethoxy)1,2,4-triazolo[1,5-a]pyrimidine-2-sulfonyl chloride

This material was prepared in 74% yield from 2-benzylthio-5-(2,2,2-trifluoroethoxy)-1,2,4-triazolo[1,5-a]pyrimidine following the general procedure described in Examples 38–45. The product was isolated as a solid, mp 91°–96° C. IR and [1]H NMR spectra were in agreement with the assigned structure.

Exact mass calculated for $C_7H_4ClF_3N_4O_3S$: 315.9655

Found: 315.9650

EXAMPLE 54

Preparation of 5-ethoxy-1,2,4-triazolo[1,5-a]pyrimidine-2-sulfonyl chloride

This material was prepared in 74% yield from 2-benzylthio-5-ethoxy-1,2,4-triazolo[1,5-a]pyrimidine following the general procedure described in Examples 38–45. The product was isolated as a solid, mp 91°–96° C. IR and [1]H NMR spectra were in agreement with the assigned structure.

EXAMPLE 55

Preparation of 5-methoxy-6-methyl-1,2,4-triazolo[1,5-a]pyrimidine-2-sulfonyl chloride

This material was prepared in 80% yield from 2-benzylthio-5-methoxy-6-methyl-1,2,4-triazolo[1,5-a]-pyrimidine following the general procedure outlined in Examples 38–45. The produce was isolated as a solid, mp 154°–157° C. IR and [1]H NMR spectra were in agreement with the assigned structure.

Analysis:

Calculated for $C_7H_7ClN_4O_3S$: C, 32.00; H, 2.67; N, 21.33.

Found: C, 32.35; H, 2.61; N, 21.45.

EXAMPLE 56

Preparation of 6-ethoxycarbonyl-7-methyl-1,2,4-triazolo[1,5-a]pyrimidine-2-sulfonyl chloride

This material was prepared in 82% yield from 2-benzylthio-6-ethoxycarbonyl-7-methyl-1,2,4-triazolo-[1,5-a]pyrimidine following the general procedure described in Example 46. The product was isolated as a solid, mp 65°–69° C. IR and [1]H NMR spectra were in agreement with the assigned structure.

Analysis:

Calculated for $C_9H_9ClN_4O_4S$: C, 35.47; H, 2.95; N, 18.39

Found: C, 36.04; H, 3.02; N, 18.27

EXAMPLE 57

Preparation of 6-(4-nitrophenyl)-1,2,4-triazolo[1,5-a]pyrimidine-2-sulfonyl chloride

This material was prepared in 71% yield from 2-benzylthio-6-(4-nitrophenyl)-1,2,4-triazolo[1,5-a]-pyrimidine following the general procedure described in Examples 38–45. The product was isolated as a solid, mp 159°–167° C. IR and [1]H NMR spectra were in agreement with the assigned structure.

EXAMPLE 58

Preparation of 5,7-dimethyl-N-(2-chlorophenyl)-1,2,4-triazolo[1,5-a]pyrimidine-2-sulfonamide

To a solution of 0.74 ml (0.90 g, 7.0 mmol) of o-chloroaniline in 10 ml of dry pyridine was added 1.89 g (7.66 mmol) of the sulfonyl chloride prepared in Example 38. The resulting dark solution was stirred at ambient temperature for 18 hours and evaporated to dryness. The residue was treated with 15 ml of 1N NaOH and charcoal and stirred for 15 minutes. The mixture was filtered through celite and the filrate was acidified with 3N HCl to precipitate the product. Filtration and drying in vacuo gave the desired product (2.01 g, 85%) as a light brown solid, m.p. 188°–189.5° C. IR and [1]H NMR spectra were in agreement with the desired compound of formula I (Ar=o-chlorophenyl, X=Z=Me, Y=H).

Analysis:

Calculated for $C_{13}H_{12}ClN_5O_2S$: C, 46.23; H, 3.58; N, 20.73; Cl, 10.50; S, 9.49.

Found: C, 46.09; H, 3.48; N, 20.89; Cl, 10.34; S, 9.37.

EXAMPLE 59

Preparation of methyl N-(5,7-dimethyl-1,2,4-triazolo[1,5-a]pyrimidine-2-sulfonyl)anthranilate

To a solution of 0.91 ml (1.1 g, 7.0 mmol) of methyl anthranilate in 10 ml of dry pyridine was added 1.89 g (7.66 mmol) of the sulfonyl chloride prepared in Example 38. The resulting dark solution was stirred at room temperature for 18 hours and evaporated to dryness. The residue was treated with 15 ml of 1N NaOH and charcoal and stirred for 15 minutes. The mixture was filtered through celite, and the filtrate was acidified with 3N HCl to precipitate the product. The product was collected by filtration and dried in vacuo to yield 2.27 g (90%) of the desired product of Formula I (X=Z=Me, Y=H, Ar=o-carbomethoxyphenyl) as a cream colored solid, m.p. 169.5°-170.5° C. IR and [1]H NMR spectra confirmed the structure of the product.

Analysis:

Calculated for $C_{15}H_{15}N_5O_4S$: C, 49.86; H, 4.18; N, 19.38; S, 8.87.

Found: C, 49.68; H, 4.13; N, 19.35; S, 8.69.

EXAMPLE 60

Preparation of 5,7-dimethyl-N-(2,6-dimethylphenyl)-1,2,4-triazolo[1,5-a]pyrimidine-2-sulfonamide

A solution of 2.2 g (8.9 mmol) of 5,7-dimethyl-1,2,4-triazolo[1,5-a]pyrimidine-2-sulfonyl chloride, 1.01 ml (8.4 mmol) of 2,6-dimethylaniline, 0.7 ml (8.4 mmol) of dry pyridine and 4 mg of DMAP in 20 ml of CH_2Cl_2 was stirred at room temperature for 17 hours. The solvent was removed by evaporation and the residue was taken up in 0.5M NaOH. The solution was extracted with diethyl ether and the aqueous phase was acidified with 3N HCl to precipitate a solid. The solid was collected by filtration and dried in vacuo to yield 2.72 g (97 percent) of the desired product as a white solid, m.p. 263°-266° C. (decomp.): [1]H NMR (DMSO-d_6)δ10.4 (1H, broad S), 7.55 (1H, s), 7.2 (3H, s), 2.7 and 2.8 (3H each, s) and 2.1 (6H, s); IR (KBr) 3100, 2980-2780, 1628, 1540 and 1355 cm^{-1}.

Analysis:

Calculated for $C_{15}H_{17}N_5O_2S$: C, 54.31; H, 5.23; N, 21.23.

Found: C, 53.59; H, 5.07; N, 20.65.

EXAMPLE 61

Preparation of 6,7-cyclopentano-5-methyl-N-(2,6-dichlorophenyl)-1,2,4-triazolo[1,5-a]pyrimidine-2-sulfonamide

A solution of 3.31 g (12.1 mmol) of crude 6,7-cyclopentano-5-methyl-1,2,4-triazolo[1,5-a]pyrimidine-2-sulfonyl chloride and 1.87 g (11.6 mmol) of 2,6-dichloroaniline in 15 ml of dry pyridine was stirred at 45°-50° C. for 23 hours. The majority of the pyridine was removed by evaporation at reduced pressure, and the residue was treated with 25 ml of 1N NaOH and ice. After stirring for 15 minutes, the mixture was filtered and the filtrate was acidified with 3N HCl to precipitate a light brown solid. The solid was taken up in 0.5N NaOh and filtered. The filtrate was acidified with 3N HCl to precipitate a solid. The solid was collected by filtration and dried in vacuo to yield 1.19 g (26 percent) of the desired sulfonamide as a light brown solid, m.p. 264°-266° C.: [1]H NMR (DMSO-d_6) δ10.83 (1H, broad s), 7.1-7.6 (3H, m) and 2.0-3.6 (9H, m including s at 2.57); IR (KBr) 3410, 1620, 1549, 1442, 1399, 1358 and 1167^{-1}.

Analysis:

Calculated for $C_{15}H_{13}Cl_2N_5O_2S$: C, 45.24; H, 3.29; N, 17.58.

Found: C, 45.47; H, 3.18; N, 17.41.

EXAMPLE 62

Preparation of 5,7-dmethyl-N-(2,4,6-trichlorophenyl)-1,2,4-triazolo[1,5-a]pyrimidine-2-sulfonamide

A solution (10.7 ml, 17.1 mmol) of 1.60 M N-butyllithium in hexane was added to a solution of 3.20 g (16.3 mmol) of 2,4,6-trichloroaniline in 20 ml of dry THF cooled to −78° C. The resultant solution was then allowed to warm to room temperature. This solution was added to a solution of 2.00 g (8.11 mmol) of 5,7-dimethyl-1,2,4-triazolo[1,5-a]pyrimidine-2-sulfonyl chloride in 30 ml of dry THF cooled to −10° C. The temperature of the reaction mixture was maintained between −13° C. and −19° C. during to course of the addition. After the addition was complete, the reaction mixture was stirred for 30 minutes and warmed to room temperature. After 1 hour at room temperature, THF was removed from the reaction mixture by evaporation. The residue was triturated with H_2O and filtered. The filtrate was treated with charcoal and filtered through celite. The filtrate was washed with Et_2O, and the aqueous phase was separated and acidified with 3N HCl to precipitate a solid. The solid was collected by filtration, washed with water and drid in vacuo to yield 0.70 g (21%) of the desired product as a tan solid, m.p. >200° C. (decomp.) [1]H NMR and IR spectra were consistent with the assigned structure.

Analysis:

Calculated for $C_{13}H_{10}N_5O_2S$: C, 38.40; H, 2.48; N, 17.22.

Found: C, 38.36; H, 2.48; N, 17.14.

EXAMPLE 63

Preparation of 6-chloro-N-(2,6-difluorophenyl)-1,2,4-triazolo[1,5-a]pyrimidine-2-sulfonamide

The starting 2,6-difluoroaniline (1.7 g, 13 mmol) was dissolved in 3.5 ml of pyridine and 3.5 g (14 mmol) of 6-chloro-1,2,4-triazolo[1,5-a]pyrimidine-2-sulfonyl chloride was added. After an exothermic reaction subsided the reaction mixture was heated at 60°-70° C. overnight. The solvent was removed by evaporation at reduced pressure and the residue was taken up in aqueous sodium bicarbonate. The aqueous solution was washed with ether, and acidified with acqueous HCl. The solid which separated upon acidification was collected by filtration, dried and recrystallized from methanol to afford 2.5 g (55%) of the desired product as a crystalline solid, mp 224°-226° C. IR and [1]H NMR spectra were in agreement with the assigned structure.

Analysis:

Calculated for $C_{11}H_6ClF_2N_5O_2S$: C, 38.21; H, 1.75; N, 20.26.

Found: C, 38.32; H, 1.44; N, 20.18.

EXAMPLE 64

Preparation of methyl 3-methyl-N-(6-methyl-1,2,4-triazolo[1,5-a]pyrimidine-2-sulfonyl)-anthranilate

Methyl 3-methylanthranilate (2.1 g, 13 mmol) was dissolved in 4 ml pyridine and 6-methyl-1,2,4-triazolo-[1,5-a]pyrimidine-2-sulfonyl chloride was added. After a mild exothermic reaction subsided the reaction mixture was stirred at 50° C. for 24 hours. The pyridine was removed by evaporation at reduced pressure and the residue was treated with in 10% aqueous sodium bicarbonate. Insoluble material was collected by filtration, washed with ether and dried to yield 2.9 (63%) of the desired product as a solid, mp 198.5°-205° C. An analytical sample was prepared by recrystallization from ethanol to yield a crystalline solid, mp 208.5°-210.5° C. IR and [1]H NMR spectra were in agreement with the assigned structure.

Analysis: Calculated for $C_{15}H_{15}N_5O_4S$: C, 49.85; H, 4.18; N, 19.38. Found: C, 49.96; H, 4.14; N, 19.75.

EXAMPLE 65

Preparation of 5-methyl-N-(2,6-difluorophenyl)-1,2,4-triazolo[1,5-a]pyrimidine-2-sulfonamide

The starting 2,6-difluoroaniline (18.1 g, 0.140 mol) was dissolved in 45 ml of pyridine and 36.1 g (0.155 mol) of 5-methyl-1,2,4-triazolo[1,5-a]pyrimidine-2-sulfonyl chloride was added. After an exothermic reaction subsided the reaction mixture was stirred at room temperature for 15.5 hours. The pyridine was removed by evaporation at reduced pressure, and the residue was treated with 600 ml of 0.5N NaOH. After stirring to dissolve all soluble material the mixture was filtered through celite and the filtrate was acifified with 3N HCl. The precipitate which separated upon acidification was collected by filtration and dried to yield 33.0 g (73%) of the desired product as a pale red solid, mp 245°-247° C. IR and ^1H NMR spectra were in agreement with the assigned structure.

Analysis: Calculated for $C_{12}H_9F_2N_5O_2S$: C, 44.31; H, 2.79; N, 21.53 Found: C, 44.69; H, 2.80; N, 21.85

EXAMPLE 66

Preparation of 5,7-dimethyl-N-(2-acetoxymethyl-6-chlorophenyl)-1,2,4-triazolo[1,5-a]pyrimidine-2-sulfonamide

A solution of 1.30 gm (6.50 mmol) of 2-amino-3-chlorobenzyl acetate, 4.11 gm (52.0 mmol) of pyridine and 5.0 ml of acetonitrile was treated with 1.61 gm (6.50 mmol) of 5,7-dimethyl-1,2,4-triazolo[1,5-a]pyrimidine-2-sulfonyl chloride and the resulting mixture stirred at 25° C. for 120 hours. An additional 0.53 gm (2.2 mmol) of the sulfonyl chloride was added and stirring at 25° C. continued for an additional 24 hours. The mixture was filtered and the filtrate evaporated to provide a brown oil. The oil was then dissolved in 40 ml of methylene chloride and stirred with 25 ml of 0.5M NaOH. After 5 minutes, the aqueous phase was separated, washed with ether and acidified with 3N HCl. A light brown solid was collected, washed with water, dried and recrystallized from acetonitrile to provide 0.35 gm (13%) of the desired product as a solid, mp 214°-217° C., containing approximately 10% of an impurity. IR and ^1H NMR spectra were in agreement with the assigned structure.

Analysis: Calculated for $C_{16}H_{16}ClN_5O_4S$: C, 46.89; H, 3.94; N, 17.08. Found: C, 46.60; H, 3.80; N, 17.73.

EXAMPLE 67

Preparation of methyl 3-amino-2-bromo-4-methyl-N-(5,7-dimethyl-1,2,4-triazolo-[1,5-a]pyrimidine-2-sulfonyl)benzoate

A solution of 1.50 g (6.15 mmol) of methyl 2-bromo-3-amino-4-methylbenzoate in 7 ml of pyridine was treated with 1.67 g (6.76 mmol) of 5,7-dimethyl-1,2,4-triazolo[1,5-a]pyrimidine-2-sulfonyl chloride. After stirring at 25° C. for 18 hours an additional 0.46 g (1.9 mmol) of the sulfonyl chloride was added and the reaction mixture was heated at 52°-55° C. for 3 hours. The solvent was removed by evaporation and the residue was partitioned between methylene chloride and dilute aqueous HCl. The organic phase was washed with water, dried and evaporated at reduced pressure to yield 1.85 g (66%) of the desired product as a yellow solid upon trituration with ethyl acetate. An analytical sample was prepared by recrystallization from acetonitrile-DMF to afford a crystalline solid, mp 229°-231° C. IR and ^1H NMR spectra were in agreement with the assigned structure.

Analysis: Calculated for $C_{16}H_{16}BrN_5O_4S$: C, 42.30; H, 3.55; N, 15.41 Found: C, 42.29; H, 3.45; N, 15.68

EXAMPLE 68

Preparation of 3-amino-2-bromo-4-methyl-N-(5,7-dimethyl-1,2,4-triazolo[1,5-a]pyrimidine-2-sulfonyl)benzoic acid

A solution of 2.78 g (6.12 mmol) of methyl 3-amino-2-bromo-4-methyl-N-(5,7-dimethyl-1,2,4-triazolo[1,5-a]pyrimidine-2-sulfonyl)benzoate and 30 ml of 5% aqueous NaOH in 30 ml of water was stirred at 25° C. for 2.5 hours. The reaction mixture was filtered and the filtrate was cooled in ice and acidified to approximately pH 2 with 3N HCl. The solid which separated was collected by filtration, washed with water and dried in vacuo to yield 2.10 g (78%) of the desired product as a gold solid, mp 290° C. (decomposition). IR and ^1H NMR spectra were in agreement with the assigned structure.

Analysis: Calculated for $C_{15}H_{14}BrN_5O_4S$: C, 40.92; H, 3.21; N, 15.90 Found: C, 40.51; H, 3.11; N, 16.01.

EXAMPLE 69

Preparation of 5-methylthio-N-(2,6-dichlorophenyl)-1,2,4-triazolo[1,5-a]pyrimidine-2-sulfonamide

To 25 ml (13 mmol) of a 0.52M solution of sodium methyl mercaptide in DMSO prepared by bubbling methyl mercaptan into a suspension of sodium hydride in DMSO, was added 2.6 g (5.9 mmol) of 5-(2,2,2-trifluoroethoxy)N-(2,6-dichlorophenyl)-1,2,4-triazolo[1,5-a]pyrimidine-2-sulfonamide. The solution was stirred at room temperature for 25 hours, diluted with 100 ml of ice water and neutralized with 3N aqueous HCl. The gummy solid which separated was collected and taken up in 0.5N aqueous NaOH. The mixture was filtered to remove insoluble material, and the filtrate was acidified with 6N aqueous HCl. The solid which separated was collected by filtration and dried to yield 1.5 g (66%) of the desired product as a pale yellow solid, mp 239°-243° C. IR and ^1H NMR spectra were in agreement with the assigned structure.

Analysis: Calculated for $C_{12}H_9Cl_2N_5O_2S_2$: C, 36.92; H, 2.31; N, 17.95. Found: C, 36.51; H, 2.41; N, 17.68.

EXAMPLE 70

Preparation of 5-dimethylamino-N-(2,6-dichlorophenyl)-1,2,4-triazolo[1,5-a]pyrimidine-2-sulfonamide.

The starting 5-(2,2,2-trifluoroethoxy)-N-(2,6-dichlorophenyl)-1,2,4-triazolo[1,5-a]pyrimidine-2-sulfonamide (1.5 g, 3.4 mmol) was dissolved in 5 ml (44 mmol) of 50% aqueous dimethylamine. After stirring for 48 hours at room temperature the solution was diluted with water and acidified with 6N aqueous HCl. The solid which separated was collected by filtration and treated with 0.5N aqueous NaOH and filtered to remove insoluble material. The filtrate was acidified to precipitate a solid. The solid was collected and dried to yield 1.0 g (60%) of the desired product as a solid, mp >310° C. IR and ^1H NMR spectra were in agreement with the assigned structure.

Analysis: Calculated for $C_{13}H_{12}Cl_2H_6O_2S$: C, 40.31; H, 3.10; N, 21.71; S, 8.28. Found: C, 40.08; H, 3.05; N, 22.33 S, 7.99.

EXAMPLE 71

Preparation of 6-bromo-5-methyl-N-(2,6-dichlorophenyl)-1,2,4-triazolo[1,5-a]pyrimidine-2-sulfonamide

A suspension of 4.0 g (11 mmol) of 5-methyl-N-(2,6-dichlorophenyl)-1,2,4-triazolo[1,5-a]pyrimidine-2-sulfonamide in 50 ml of glacial acetic acid and 10 ml of acetic anhydride was stirred at 90° C. for 30 minutes. N-Bromosuccinimide (2.4 g, 13 mmol) was added to this hot solution, and the reaction mixture was stirred at 90° C. for 60 minutes. The solution was cooled and poured into 200 ml of ice water. A solid which separated was collected and dried. This crude product was purified by dissolving the sample in methylene chloride, filtering the solution through silica gel and triturating the fitrate with pentane. The desired product was obtained as a solid, mp 215°-216° C. IR and ^{1}H NMR spectra were in agreement with the assigned structure.

Exact mass calculated for $C_{12}H_8BrCl_2N_5O_2S$: 438.8898 Found: 438.8899

EXAMPLE 72

Preparation of 5,7,N-trimethyl-N-(2,6-dichlorophenyl)-1,2,4-triazolo[1,5-a]-pyrimidine-2-sulfonamide

A mixture of 3.00 g (8.06 mmol) of 5,7-dimethyl-N-(2,6-dichlorophenyl)-1,2,4-triazolo[1,5-a]-pyrimidine-2-sulfonamide and 0.90 g (8.1 mmol) of potassium t-butoxide in 30 ml of acetonitrile was heated at reflux for 40 minutes. After cooling to room temperature 1.14 g (8.06 mmol) of methyl iodide was added, and the reaction was heated at reflux for 1 hour. After cooling to room temperature, the reaction mixture was diluted with methylene chloride and washed with 1% aqueous NaOH. The organic phase was separated, dried ($MgSO_4$) and evaporated at reduced pressure. The brown solid residue was recrystallized from acetone to give 1.60 g (51%) of the desire product as a tan solid, mp 220°-222° C. IR and ^{1}H NMR spectra were in agreement with the assigned structure.

Analysis:

Calculated for $C_{14}H_{13}Cl_2N_5O_2S$: C, 43.54; H, 3.39; N, 18.13

Found: C, 43.55; H, 3.32; N, 18.03

EXAMPLE 73

Preparation of 5-methyl-N-benzoyl-N-(2,6-dichlorophenyl)-1,2,4-triazolo[1,5-a]-pyrimidine-2-sulfonamide

A mixture of 3.00 g (8.37 mmol) of 5-methyl-N-(2,6-dichlorophenyl)-1,2,4-triazolo[1,5-a]pyrimidine-2-sulfonamide and 1.16 g (8.37 mmol) of anhydrous powdered K_2CO_3 in 100 ml of acetone was heated at reflux for 30 minutes. A solution of 1.18 g (8.37 mmol) of benzoyl chloride in 10 ml of acetone was added, and the reaction was heated at reflux for 115 min. The reaction was filtered, and the filtrate was evaporated at reduced pressure. The solid residue was collected by filtration, washed thoroughly with aqueous $NaHCO_3$ and H_2O and dried to yield 2.75 g (72%) of the desired product as a solid, mp 187°-189° C. IR and ^{1}H NMR spectra were in agreement with the assigned structure.

Analysis:

Calculated for $C_{19}H_{13}Cl_2N_5O_3S$: C, 49.36; H, 2.83; N, 15.15.

Found: C, 48.97; H, 2.84; N, 15.16

EXAMPLE 74

Preparation of 5-methyl-N-(2,6-dichlorophenyl)-4,5,6,7-tetrahydro-1,2,4-triazolo[1,5-a]pyrimidine-2-sulfonamide

Sodium borohydride (0.6 g, 16 mmol) was added to a solution of 3.0 g (8.3 mmol) of 5-methyl-N-(2,6-dichlorophenyl)-1,2,4-triazolo[1,5-a]pyrimidine-2-sulfonamide in 25 ml of dry DMSO. An exothermic reaction occurred and 2.0 ml (31 mmol) of methanesulfonic acid in 5 ml of DMSO was added at a rate to maintain the temperature of the reaction mixture at 60° C. After the addition was complete the reaction mixture was stirred for 10 minutes and carefully quenched with 0.5N aqueous NaOH. The clear yellow solution was filtered, and the filtrate was acidified with 3N aqueous HCl. The resutling precipitate was treated with dilute aqueous NaOH and filtered to remove insoluble material. The filtrate was acidified with aqueous HCl to precipitate a solid. The solid was collected by filtration and dried to yield 1.11 g (37%) of the desired product as a solid, mp 230°-235° C. IR and ^{1}H NMR spectra were in agreement with the assigned structure.

Analysis:

Calculated for $C_{12}H_{12}Cl_2N_5O_2S$: C, 39.89; H, 3.32; N, 19.39.

Found: C, 39.72; H, 3.42; N, 19.19.

EXAMPLE 75

Preparation of N-(2,6-dichloro-3-methylphenyl)-5-amino-1,2,4-triazole-3-sulfonamide

Potassium hydroxide (72.9 g of 85 percent pellets, 1.20 mol) was dissolved in one liter of water in a 2 liter round bottom flask and 113.3 g (0.30 mol) of wet N-(2,6-dichloro-3-methylphenyl)-5,7-dimethyl-1,2,4,-triazolo[1,5-a]pyrimidine-2-sulfonamide was added with stirring. The mixture obtained was cooled to 17° C. and 100 ml of 30 percent hydrogen peroxide solution (about 1 mole) was added with stirring over a 0.5 hour period so that the temperature did not exceed 40° C. The reaction was found to be complete after three hours by high pressure liquid chromatography. An aqueous solution of sodium bisulfite was added to quench the excess hydrogen peroxide and the solution obtained was filtered through celite and then acidified with concentrated hydrochloric acid. The precipitate that formed was collected by filtration, washed with water, and partially dried. This material, which is the N^1-acetyl derivative of the desired product, was dissolved in 800 ml of tetrahydrofuran and the resulting solution was combined with 100 ml of water and 100 ml of concentrated hydrochloric acid. This mixture was heated at reflux with stirring in a two liter round bottom flask overnight. The solvent was removed by evaporation under reduced pressure and the resulting aqueous suspension was filtered to collect the solid product. This was washed with water and dried to obtain 59.3 g (61 percent of theory) of the title compound as a white solid. This compound has an m.p. of 206°-8° C.

Analysis:

Calculated for $C_9H_9Cl_3N_5O_2S$: C, 30.1; H, 2.81; N, 19.3.

Found: C, 29.9; H, 3.33; N, 19.0.

EXAMPLE 76

Preparation of N-(2-trifluoromethylphenyl)-5-amino-1,2,4-triazole-3-sulfonamide

A 110.6 g (0.30 mol) portion of N-(2-trifluoromethylphenyl)-5,7-dimethyl-1,2,4,-triazolo[1,5-a]pyrimidine-2-sulfonamide was added to a solution of 79 g of 85 percent potassium hydroxide (1.2 mol) in two liters of water. Another liter of water was added and then 400 ml of 30 percent hydrogen peroxide (3.9 moles) was added to the mixture with stirring and cooling with an ice bath at a rate so that the temperature did not exceed 40° C. After about 3.5 hours, the reaction was found to be complete by thin layer chromatography. About 100 ml of 12N hydrochloric acid was added dropwise to precipitate the product and then a little solid sodium bisulfite was added to destroy the excess hydrogen peroxide. The precipitate was collected by filtration washed with water and dried to obtain 94 g of the N^1-acetyl derivative of the desired product. This was dissolved in 750 ml of tetrahydrofuran and 375 ml of concentrated hydrochloric acid and 360 ml of water were added. The mixture was heated to reflux with stirring for about four hours. The solvent was then removed by evaporation under reduced pressure. Ethanol was added and the solution obtained was treated with charcoal. Ethanol was evaporated to precipitate the title compound which was collected by filtration and dried to obtain a total of 51.6 g (56.4 percent of theory) of white solid, the first 47.6 g of which melted at 227°-9° C.

Analysis:

Calculated for $C_9H_8N_5F_3SO_2$: C, 35.18; H, 2.62; N, 22.80; S, 10.43.

Found: C, 34.79; H, 2.65; N, 22.53; S, 10.20.

EXAMPLE 77

Preparation of N-(2,6-dichloro-3-methylphenyl)-7-hydroxy-5-methyl-1,2,4-triazolo[1,5-a]-pyrimidine-2-sulfonamide

A solution of 32.2 g (0.10 mol) of N-(2,6-dichloro-3-methylphenyl)-5-amino-1,2,4-triazole-3-sulfonamide and 14 ml (0.11 mol) of ethyl acetoacetate in 500 ml of methanol containing 1 ml of 12N hydrochloric acid was heated to reflux with stirring for about 18 hours. The solid present was collected by filtration and the filtrate was heated to reflux for another day. The mixture obtained was cooled in an ice bath and the solid present was collected by filtration. The filtrate was concentrated to about 200 ml by evaporation of methanol and heated to reflux overnight. The mixture obtained was filtered to collect the solid present. The filtrate was concentrated to about 150 ml, treated with about 2 ml of ethyl acetoacetate, and heated at reflux for about 3 days. The solids present were collected by filtration and dried to obtain 6.4 g, 10.0 g, 8.2 g and 11.1 g crops of the title compound for a total of 35.7 g (92 percent of theory). The first obtained crop melted at 346°-7° C. with decomposition.

Analysis:

Calculated for $C_{13}H_{11}Cl_2N_5O_3S$: C, 40.2; H, 2.86; N, 18.04

Found: C, 39.6; H, 2.96; N, 17.96

EXAMPLE 78

Preparation of N-(2-trifluoromethylphenyl)-7-hydroxy-5-methyl-1,2,4-triazolo[1,5-a]pyrimidine-2-sulfonamide

A solution of 1 ml of 12N hydrochloric acid in 250 ml of methanol was added to a mixture of 20.0 g (65.1 mmol) of N-(2-trifluoromethylphenyl)-5-amino-1,2,4-triazole-3-sulfonamide and 9.2 ml (72.2 mmol) of ethyl acetoacetate and the mixture heated to reflux with stirring. After about 5 days, most but not all of the starting material was found to have reacted by thin layer chromatography. The solution was chilled and the precipitate that formed was collected by filtration, washed with cold methanol and dried to obtain 16.5 g (67.9 percent of theory) of the title compound as a white solid hemihydrate melting at 245°-7° C.

Analysis:

Calculated for $C_{13}H_{10}F_3N_5O_3.\frac{1}{2}H_2O$: C, 40.8; H, 2.88; N, 18.31; S, 8.37.

Found: C, 40.4; H, 2.76; N, 18.29; S, 7.93

EXAMPLE 79

Preparation of N-(2,6-dichloro-3-methylphenyl)-7-chloro-5-methyl-1,2,4-triazolo-[1,5-a]pyrimidine-2-sulfonamide

A solution of 100 ml of phosphoryl chloride in 400 ml of dry acetonitrile was added to 12.0 g (30.9 mmol) of N-(2,6-dichloro-3-methylphenyl)-7-hydroxy-5-methyl-1,2,4-triazolo[1,5-a]pyrimidine-2-sulfonamide and heated to reflux with stirring. After about 24 hours, the mixture became a solution which appeared to contain little or no starting material by thin layer chromatography. The volatiles were largely removed by evaporation under reduced pressure and the residue poured onto about one liter of ice and water with stirring using fresh acetonitrile as a transfer solvent. The solid in the resulting mixture was collected by filtration, washed with water, and dried under reduced pressure at 70° C. overnight. The resulting solid, which was found to be the title compound by NMR analysis, amounted to 8.4 g (67 percent of theory).

EXAMPLE 80

Preparation of N-(2-trifluoromethylphenyl)-7-chloro-5-methyl-1,2,4-triazolo[1,5-a]pyridmidine-2-sulfonamide

Phosphorus oxychloride (135 ml, 1.47 mol) was diluted with 335 ml of dry acetonitrile and added to 15 g (40 mmol) of N-(2-trifluoromethylphenyl)-7-hydroxy-5-methyl-1,2,4-triazolo[1,5-a]pyrimidine-2-sulfonamide in a one liter flask and heated to reflux with stirring.

After about 3 days, the reaction was found to be complete by thin layer chromatography. Volatiles were removed by evaporation under reduced pressure until the mixture became very viscous and the residue was poured onto about one liter of ice and water with stirring. After about 30 minutes, the solid that formed was collected by filtration, washed with ice water, and dried under reduced pressure at room temperature. It was then dissolved in methylene chloride and the resulting solution dried over magnesium sulfate for about five minutes and filtered. The volatiles were removed from the filtrate by evaporation under reduced pressure to obtain the title compound as a white solid residue. The product, the structure of which was confirmed by

NMR analysis, amounted to 13.4 g (85.4 percent of theory).

EXAMPLE 81

Preparation of N-(2,6-dichloro-3-methylphenyl)-7-methoxy-5-methyl-1,2,4-triazolo[1,5-a]pyrimidine-2-sulfonamide

Sodium (0.6 g, 26 mmol) was added to about 40 ml of methanol and allowed to react. N-(2,6-dichloro-3-methylphenyl)-7-chloro-5-methyl-1,2,4-triazolo[1,5-a]pyrimidine-2-sulfonamide (2.5 g, 6.9 mmol) was added with stirring. After about 90 minutes, thin layer chromatography indicated the starting material had reacted. The solution was then acidified by adding 6N hydrochloric acid dropwise and then concentrated by evaporation under reduced pressure. The residue was triturated with water and the solid that formed was washed with water and dried to obtain 1.35 g of the title compound as a white solid, m.p. 239°–42° C.

Analysis: Calculated for $C_{14}H_{13}Cl_2N_5O_3$: C, 41.8; H, 3.26; N, 17.41; S, 7.97. Found: C, 41.4; H, 3.19; N, 17.42; S, 8.15.

EXAMPLE 82

Preparation of N-(2,6-dichloro-3-methylphenyl)-7-ethoxy-5-methyl-1,2,4-triazolo[1,5-a]pyridimidine-2-sulfonamide

Sodium (0.69 g, 30 mmol) was added to about 5 ml of ethanol and allowed to react. The mixture was allowed to cool and then 4.0 g (9.8 mmol) of N-(2,6-dichloro-3-methylphenyl)-7-chloro-5-methyl-1,2,4-triazolo[1,5-a]pyrimidine-2-sulfonamide was added with stirring. After 15 minutes no starting material remained by thin layer chromatographic analysis although complete solution was never attained. The mixture was acidified with 6N hydrochloric acid and concentrated under reduced pressure. The residue was triturated with water and the solid removed by filtration and washed with water. It was then dissolved in aqueous sodium hydroxide using a minimum amount of the base and the aqueous solution was twice extracted with ether and acidified with 6N hydrochloric acid. The solid that formed was collected by filtration, washed with water, and dried. This was extracted with about 500 ml of boiling chloroform. The chloroform solution was concentrated to about 150 ml and allowed to cool to form a precipitate which was collected by filtration and dried to obtain 1.7 g (42 percent of theory) of the title compound as a white solid, m.p. 228°–9° C.

Analysis: Calculated for $C_{15}H_{15}Cl_2N_5O_3S$: C, 43.3; H, 3.63; N, 16.83; S, 7.70. Found: C, 42.9; H, 3.66; N, 16.92; S, 7.66.

EXAMPLE 83

Preparation of N-(2,6-dichlorophenyl)-7-methylthio-5-methyl-1,2,4-triazolo[1,5-a]pyrimidine-2-sulfonamide

An oil dispersion of sodium hydride (1.15 g, 24 mmol) was washed three times with hexane by slurrying and decanting and was then suspended in 30 ml of dry dimethyl sulfoxide. An excess of methanethiol (greater than 1.3 ml) was added dropwise with stirring. A solution of N-(2,6-dichlorophenyl)-7-chloro-5-methyl-1,2,4-triazolo[1,5-a]pyrimidine-2-sulfonamide (3.14 g, 8.0 mmol) was added to this dropwise with stirring. Thirty minutes after the addition was complete, about 200 ml of water were added and the solution was acidified with 6N hydrochloric acid. Nitrogen was blown through the system to remove any unreacted methanethiol (trapped in sodium hypochlorite solution) and the solid present was collected by filtration, washed with water, and dried to obtain 2.7 g (84 percent by theory) of the title compound contaminated with some 5-hydroxy analog. A 1 g portion of this was dissolved in aqueous sodium hydroxide (minimum amount of base) and the resulting solution was treated with charcoal, filtered, and then acidified with 6N hydrochloric acid. The resulting precipitate was collected by filtration, washed with water, and dried to obtain 0.9 g of the title compound melting at 289°–91° C.

Analysis: Calculated for $C_{13}H_{11}Cl_2N_5O_2S_2$ C, 38.6; H, 2.74; N, 17.32. Found: C, 38.4; H, 2.65; N, 17.20.

EXAMPLE 84

Preparation of N-(2-trifluorophenyl)-7-methylthio-5-methyl-1,2,4-triazolo[1,5-a]-pyrimidine-2-sulfonamide

Sodium hydride (1.2 g, 25 mmol) was washed three times with hexane and suspended in 50 ml of dry dimethyl sulfoxide. An excess of methanethiol (greater than 1.4 ml) was added dropwise until a clear solution formed. The solution was allowed to cool and then 2.5 g (6.4 mmol) of N-(2-trifluorophenyl)-7-chloro-5-methyl-1,2,4-triazolo[1,5-a]pyrimidine-2-sulfonamide was added. After a short time, the starting material was found to be consumed using thin layer chromatography and the solution was diluted with water and acidified with hydrochloric acid. Nitrogen was blown through the solution to remove any unreacted methanethiol. The solids in the resulting mixture were collected by filtration, washed with water, dissolved in dilute aqueous sodium hydroxide, and reprecipitated with 6N hydrochloric acid. The solid was collected by filtration, washed with water, and dried to obtain 1.4 g (54 percent of theory) of the title compound contaminated with some hydroxy analog and melting at 184°–9° C. A portion of this was extracted with boiling chloroform and the chloroform solution was concentrated by evaporation and then diluted with carbon tetrachloride and cooled to precipitate the title compound. This melted at 193°–200° C. after collection and drying.

Analysis: Calculated for $C_{14}H_{12}F_3N_5O_2S_2$: C, 41.7; H, 3.00; N, 17.36; S, 15.90. Found: C, 41.4; H, 2.95; N, 17.21 S, 15.65.

EXAMPLE 85

Preparation of N-(2,6-dichloro-3-methylphenyl)-5,7-dihydroxy-1,2,4-triazolo[1,5-a]pyrimidine-2-sulfonamide

Sodium (3.11 g, 135 mmol) was added to 250 ml of absolute ethanol in a 500 ml round bottom flask and allowed to react under nitrogen. N-(2,6-dichloro-3-methylphenyl)-5-amino-1,2,4-triazole-3-sulfonamide (14.5 g, 45 mmol) and then dimethyl malonate (11.9 g, 90 mmol) were added and the mixture heated at reflux with stirring for about three days. The mixture was then cooled with an ice bath and filtered to collect the solids. These were washed with hexane and dissolved in about 75 ml of cold water and the resulting solution was acidified to about pH 2 with conc. hydrochloric acid. The precipitate that formed was collected by filtration and dried to obtain 13.55 g (77.1 percent of theory) of the title compound as a white powder, which decomposes above 200° C. This was shown to be the title compound by NMR.

EXAMPLE 86

Preparation of N-(2-methoxy-6-trifluoromethylphenyl)-5,7-dihydroxy-1,2,4-triazolo[1,5-a]pyrimidine-2-sulfonamide

Sodium (5.90 g, 257 mmol) was added to 250 ml of absolute ethanol under nitrogen and allowed to react. A 28.67 g, 85.0 mmol sample of N-(2-methoxy-6-trifluoromethylphenyl)-5-amino-1,2,4-triazole-3-sulfonamide and 24.46 g (170 mmol) of dimethyl malonate were added and the mixture heated at reflux with stirring for two days. It was then cooled with an ice bath and the solids present were collected by filtration and washed with hexane. They were then dissolved in about 150 ml of ice water and acidified with conc. hydrochloric acid to obtain 11.95 g, the title compound, which was collected by filtration and dried. The ethanolic solution was concentrated by evaporation and dried by adding toluene and removing volatiles by evaporation under reduced pressure three times. The residue was taken up in ethanol and treated as before with sodium and 16.85 g of dimethyl malonate to obtain another 10.26 g of the title compound. A total of 22.21 g (64.5 percent of theory) of the title compound, which melts at 237°-243° C. with decomposition, was obtained.

EXAMPLE 87

Preparation of N-(2,6-dichloro-3-methylphenyl)-5,7-dichloro-1,2,4-triazolo[1,5-a]pyrimidine-2-sulfonamide

29.27 g (75 mmol) sample of N-(2,6-dichloro-3-methylpheny)-5,7-dihydroxy-1,2,4-triazolo[1,5-a]pyrimidine-2-sulfonamide was added to 250 ml of phosphorus oxychloride and 5.0 g of phosphorus pentachloride and the mixture was heated to reflux with stirring. After 2.5 hours the mixture was allowed to cool and, after standing overnight, it was further cooled in an ice bath. The solids present were removed by filtration, washed with cold toluene, triturated with cold water, and dried to obtain 11.76 g (37 percent of theory) of the title compound; m.p. 269°-271° C. Additional material was recovered from the phosphorus oxychloride by the addition of water.

Analysis: Calculated for $C_{12}H_7Cl_4NO_2S$: C, 33.8; H, 1.65; N, 16.40. Found: C, 33.9; H, 1.70; N, 16.56.

EXAMPLE 88

Preparation of N-(2-methoxy-6-trifluoromethylphenyl)-5,7-dichloro-1,2,4-triazolo[1,5-a]pyrimidine-2-sulfonamide

A 2.03 g (5.0 mmol) sample of N-(2-methoxy-6-trifluoromethylphenyl)-5,7-dihydroxy-1,2,4-triazolo[1,5-a]pyrimidine-2-sulfonamide was combined with 15 ml of phosphorus oxychloride and the mixture heated to reflux with stirring for eight hours. The mixture was allowed to cool and the solids present were collected by filtration and washed with cold toluene. They were then washed with water and dried to obtain 0.55 g (24.9 percent of theory) of the title compound. This material was homogeneous by chromatography and its NMR spectrum was compatible with the assigned structure. Additional product was obtained by quenching the phosphorus oxychloride solution with ice water.

EXAMPLE 89

Preparation of N-(2,6-dichloro-3-methylphenyl)-5,7-dimethoxy-1,2,4-triazolo[1,5-a]pyrimidine-2-sulfonamide

Sodium (469 mg, 20.4 mmol) was added to 25 ml of methanol under nitrogen and allowed to react. The resulting solution was allowed to cool and then 2.14 g (5.0 mmol) of N-(2,6-dichloro-3-methylphenyl)-5,7-dichloro-1,2,4-triazolo[1,5 -a]pyrimidine-2-sulfonamide were added with stirring. After about one hour, 1 ml of acetic acid was added and the mixture was poured into about 150 ml of ice water. The solid present was collected by filtration and dried to obtain 1.76 g (84.2 percent of theory) of the title compound as a white powder, m.p. 218°-221° C.

Analysis: Calculated for $C_{14}H_{13}Cl_2N_5O_4S$: C, 40.2; H, 3.13; N, 16.74. Found: C, 39.9; H, 3.15; N, 16.76.

EXAMPLE 90

Preparation of N-(2,6-dichlorophenyl)-5,7-dimethoxy-1,2,4-triazolo[1,5-a]pyrimidine-2-sulfonamide

Sodium (683 mg, 29.7 mmol) was added to 30 ml of methanol under nitrogen and allowed to react. The resulting solution was cooled and 4.06 g (9.83 mmol) of N-(2,6-dichlorophenyl)-5,7-dichloro-1,2,4-triazolo[1,5-a]-pyrimidine-2-sulfonamide were added with stirring. After one hour, 2 ml of acetic acid was added and the mixture was poured into about 150 ml of ice water. The solids present were collected by filtration and dried to obtain 3.21 g (88 percent of theory) of the title compound, which is a white powder that melts at 232°-4° C.

EXAMPLE 91

Preparation of methyl 3-amino-2,4-dichlorobenzoate

This material was prepared by chlorination of methyl 3-amino-4-chlorobenzoate with N-chlorosuccinimide. The product was isolated as a solid, m.p. 50°-52° C. The product was characterized by IR and ^1H NMR spectroscopy and combustion analysis.

EXAMPLE 92

Preparation of methyl 3-amino-2-bromo-4-methylbenzoate

A mixture of 16.5 g (100 mmol) of methyl 3-amino-4-methylbenzoate and 300 ml of CCl_4 was treated with 18.6 g (105 mmol) of N-bromosuccinimide and stirred at ambient temperature for four hours. The reaction mixture was filtered, and the filtrate was evaporated at reduced pressure to afford an amber oil. To remove material resulting from bromination at the 6-position, the crude product was taken up in 100 ml of hexane and 60 ml of ether and treated with 3.96 g (50.0 mmol) of pyridine and 3.06 g (30.0 mmol) of acetic anhydride. After stirring for three hours at 25° C., the precipitate was removed by filtration. The filtrate was evaporated at reduced pressure to yield an amber oil. The crude product was purified by HPLC to afford 14.5 g (59%) of the desired product as an amber oil. IR and ^1H NMR spectra were in agreement with the assigned structure.

Analysis: Calculated for $C_9H_{10}BrNO_2$: C, 44.29; H, 4.13; N, 5.74 Found: C, 44.14; H, 3.96; N, 5.72

EXAMPLE 93

Preparation of methyl 3-methyl-4-chloroanthranilate

This material was prepared by esterification of the corresponding anthranilic acid with HCl in methanol. The product was isolated as a solid, mp 72°-74° C.

EXAMPLE 94

Preparation of 2,6-dichloro-3-trifluoromethylaniline

This material was prepared by chlorination of 2-chloro-5-trifluoromethylaniline with N-chlorosuccinimide followed by chromatographic purification. The product was isolated as a yellow oil which was characterized by IR and ^{1}H NMR spectroscopy and combustion analysis.

EXAMPLE 95

Preparation of 4-bromo-2,3-dichloro-6-methylaniline

This material was prepared from 4-bromo-5-chloro-2-methylaniline by chlorination with N-chlorosuccinimide. The product was isolated as a solid, m.p. 66°-68° C. The product was characterized by IR and ^{1}H NMR spectroscopy and combustion analysis.

EXAMPLE 96

Preparation of 2,3-dichloro-6-methylaniline

A slurry of 6.50 g (25.5 mmol) of 2,3-dichloro-4-bromo-6-methylaniline and 8.37 g (102 mmol) of sodium acetate in 120 ml of acetic acid-ethanol (1:1, v/v) was treated with 0.65 g of 5% palladium on carbon. The mixture was hydrogenated in a Parr hydrogenation apparatus at an initial pressure of 50 psi for 10 minutes. The reaction mixture was filtered, and the filtrate was concentrated by evaporation at reduced pressure. The residue was partitioned between ether and water, and the organic layer was washed with 5% aqueous sodium hydroxide, dried and evaporated at reduced pressure. The residue was purified by Kugelrohr distillation to afford 4.00 g (89% of the desired product as a colorless oil, b.p. 60°-70° C. (0.15 mm). IR and ^{1}H NMR spectra were in agreement with the assigned structure.

Analysis: Calculated for $C_7H_7Cl_2N$: C, 47.76; H, 4.01; N, 7.95. Found: C, 48.11; H, 4.04; N, 8.19.

EXAMPLE 97

Preparation of 2-amino-3-chlorobenzyl alcohol

A solution of 28.9 g (155 mmol) of methyl 3-chloroanthranilate in 100 ml of ether was added dropwise to a stirred suspenson of 7.67 g (202 mmol) of lithium aluminum hydride in 400 ml of ether. After stirring for five hours at room temperature, the grey mixture was treated sequentially with 7.7 ml of water, 7.7 ml of 15% sodium hydroxide and 23 ml of water. The reaction mixture was filtered, and the filtrate was evaporated at reduced pressure. The oily residue was dissolved in ether, and precipitation of the product was induced by addition of hexane. The product was collected by filtration to yield a tan solid in 67% yield, mp. 56°-68° C. IR and ^{1}H NMR spectra were in agreement with the assigned structure.

Analysis:

Calculated for C_7H_8ClNO: C, 53.35; H, 5.12; N, 8.88.

Found: C, 53.16; H, 4.84; N, 9.28.

EXAMPLE 98

Preparation of 2-chloro-6-methoxymethylaniline

A solution of 4.00 g (25.4 mmol) of 2-amino-3-chlorobenzyl alcohol in 30 ml of dry THF was cooled to −78° C., treated with 16.7 ml (26.7 mmol) of 1.60M n-butyllithium in hexane, warmed to 0°-5° C., treated with 3.61 g (25.4 mmol) of methyl iodide and heated at reflux for 5.5 hours. The solvent was removed by evaporation at reduced pressure. The residue was partitioned between 175 ml of ether and water, and the organic phase was separated and dried ($MgSO_4$). The solvent was removed by evaporation at reduced pressure, and the residue was purified by HPLC eluting with EtOAc (5:95, v/v) to afford 1.1 g of the desired product as a pale brown oil. IR and ^{1}H NMR spectra were in agreement with the assigned structure.

Analysis:

Calculated for $C_8H_{10}ClNO$: C, 56.00; H, 5.87; N, 8.16.

Found: C, 56,25; H, 5.98; N, 8.28.

EXAMPLE 99

Preparation of 2-acetoxymethyl-6-chloroaniline

This material was prepared from 2-amino-3-chlorobenzyl alcohol and acetyl chloride by the general procedure outlined in Example 98. The product was isolated as an amber oil and was characterized by IR and 'H NMR spectroscopy and combustion analysis.

EXAMPLE 100

Preparation of 2-benzyloxymethyl-6-chloroaniline

This material was prepared from 2-amino-3-chlorobenzyl alcohol and benzyl bromide by the general procedure outlined in Example 98. The product was purified by Kugelrohr distillation to yield an oil, b.p. 118°-125° C. (0.1 mm). The product was characterized by IR and ^{1}H NMR spectroscopy.

EXAMPLE 101

Preparation of N-n-butoxycarbonyl-2-fluoroaniline

A solution of 2-fluoroaniline (30.0 g, 0.27 mol) and di-t-butyl carbonate (66.5 g, 0.30 mol) in 100 ml of THF was heated at reflux for 4 hours. The solvent was removed by evaporation at reduced pressure, and the residue was partitioned between 1M aqueous citric acid and ethyl acetate. The organic phase was washed with saturated aqueous NaCl. The solvent was removed to afford the desired product, which was used without further purification. IR and ^{1}H NMR spectra were in agreement with the assigned structure.

Analysis:

Calculated for $C_{11}H_{14}FNO_2$: C, 62.55; H, 6.68; N, 6.63.

Found: C, 62.45; H, 6.39; N, 6.21.

EXAMPLE 102

Preparation of 2-fluoro-6-methylaniline

A solution of 8.15 g (38.5 mmol) of N-t-butoxycarbonyl-2-fluoroaniline in 30 ml of dry THF was cooled to −70° C., and 46.3 ml (93 mmol) of 2.0M t-butyllithium in pentane was added dropwise at a rate sufficient to maintain the temperature below −65° C. When the addition was complete the reaction mixture was stirred at −70° C. for 15 minutes, warmed to −20° C. and stirred for 2.5 hours. A solution of 6.8 g (30 mmol) of methyl iodide in THF was added and the reaction was allowed to warm to room temperature. The reaction mixture was partitioned between ether and water, and the organic layer was washed with saturated aqueous NaCl and dried ($MgSO_4$). Evaporation at reduced pressure gave a yellow solid which was added to 25 ml of 3N HCl and heated at reflux for 3 hours. After cooling to room temperature the pH of the solution was adjusted to pH 7, and the solution was extracted twice with methylene chloride. The combined organic phases were washed with water and dried ($MgSO_4$). Evaporation at reduced pressure gave a yellow oil which was Kugelrohr distilled to yield 3.8 g (80%) of the desired product as a liquid, b.p. 91°-93° C. (0.1 mm). IR and ^1H NMR spectra were in agreement with the assigned structure.

Analysis:

Calculated for C_7H_8FN: C, 67.20; H, 6.45; N, 11.20.

Found: C, 67.61; H, 6.09; N, 11.53.

EXAMPLE 103

Preparation of 2-fluoro-6-methylthioaniline

This material was prepared for N-t-butoxycarbonyl-2-fluoroaniline and dimethyl disulfide following the general procedure outlined in Example 102. IR and ^1H NMR spectra of the product were consistent with the assigned structure.

EXAMPLE 104

Preparation of 2-(2-chloro-4-trifluoromethylphenoxy)nitrobenzene

A mixture of 29.4 g (0.200 mol) of 2-fluoronitrobenzene, 41.0 g (0.200 mol) of 2-chloro-4-trifluoromethylphenol and 30.0 g (0.220 mol) of K_2CO_3 in 150 ml of DMSO was heated at 100° C. for six hours. The reaction mixture was poured over ice and extracted with ether. The organic phase was washed with water and saturated aqueous NaCl and dried ($MgSO_4$). The solvent was removed by evaporation at reduced pressure to yield 56.1 g (88%) of the desired product as a yellow oil. IR and ^1H NMR spectra were in agreement with the assigned structure.

Analysis:

Calculated for $C_{13}H_7ClF_3NO_3$: C, 49.15; H, 2.22; N, 4.41.

Found: C, 49.47; H, 2.07; N, 4.13.

EXAMPLE 105

Preparation of 2-(2-chloro-4-trifluoromethylphenoxy)aniline

Raney Nickel (4.0 g) was washed with water and added to 250 ml of ethanol. To this mixture under a nitrogen blanket was added 56 g (0.18 mol) of 2-(2-chloro-4-trifluoromethyl)phenoxynitrobenzene. This mixture was hydrogenated in a Parr hydrogenation apparatus at an initial pressure of 50 psi. The catalyst was removed by filtration through celite and the filtrate was evaporated at reduced pressure to yield 49.9 g (100%) of the desired product as an amber oil. IR and ^1H NMR spectra were in agreement with the assigned structure.

Analysis:

Calculated for $C_{13}H_9ClF_3NO$: C, 54.27; H, 3.15; N, 4.87.

Found: C, 54.72; H, 3.01; N, 4.61.

EXAMPLE 106

Preparation of 2-(3-chloro-5-trifluoromethyl-2-pyridyloxy)nitrobenzene

This material was prepared in 63% yield from 3-chloro-2-fluoro-5-trifluoromethylpyridine and 2-nitrophenol following the general procedure outlined in Example 104. The product was isolated as an amber oil which was characterized by IR and ^1H NMR spectroscopy.

EXAMPLE 107

Preparation of 2-(3-chloro-5-trifluoromethyl-2-pyridyloxy)aniline

This material was prepared in 61% yield by hydrogenation of 2-(3-chloro-5-trifluoromethyl-2-pyridyloxy)-nitrobenzene following the general procedure outlined in Example 105. The crude product was recrystallized from hexane to yield the desired product as white needles, mp 133°-135° C. IR and ^1H NMR spectra were in agreement with the assigned structure.

Analysis:

Calculated for $C_{12}H_8ClF_3N_2O$: C, 49.94; H, 2.79; N, 30.50.

Found: C, 49.93; H, 2.91; N, 30.27.

EXAMPLE 108

Preparation of 2-(2-chloro-4-trifluoromethylphenoxy)-6-fluoronitrobenzene

This material was prepared in 47% yeild from 2,6-difluoronitrobenzene and 2-chloro-4-trifluoromethylphenol following the general procedure outlined in Example 104. The product was isolated as an oil which was characterized by IR and ^1H NMR spectroscopy.

EXAMPLE 109

Preparation of 2-(2-chloro-4-trifluoromethylphenoxy)-6-fluoroaniline

This material was prepared in 72% yield by hydrogenation of 2-(2-chloro-4-trifluoromethylphenoxy)-6-fluoronitrobenzene following the general procedure outlined in Example 105. The crude product was Kugelrohr distilled to yield the desired product as a liquid, bp 102°-103° C. (10 mm). IR and 'H NMR spectra were in agreement with the assigned structure.

Analysis:

Calculated for $C_{13}H_8ClF_4NO$: C, 51.09; H, 2.64; H, 9.17.

Found: C, 51.34; H, 2.41; H, 9.16.

EXAMPLE 110

Preparation of 6-methoxy-2-trifluoromethylbenzoic acid

A solution of 3-trifluoromethylanisol (50.0 g, 0.28 mole) in tetrahydrofuran was cooled to −78° C. under nitrogen atmosphere with stirring. To this solution was added n-butyl lithium (114 ml of 2.5M, 0.28 mole), dropwise at such a rate that the temperature did not exceed −65° C. When the addition was complete, the mixture was stirred at −78° C. for three hours. The mixture was then poured over a slurry of dry ice/ether and allowed to come to room temperature. The solvent was removed under reduced pressure to give a white solid. This solid was dissolved in a minimum amount of water, extracted with diethyl ether (2×100 ml) and the aqueous phase with diethyl ether (2×100 ml) and the aqueous phase was acidified to pH 2 with dilute hydrochloric acid. An oil formed and was extracted with diethyl ether, washed several times with water and dried over magnesium sulfate. The solvent was removed to give 45.6 g (74 percent of theory) of the title compound as a white solid of m.p. 129°-130° C.

Analysis:

Calculated for $C_9H_7F_3O_3$: C, 49.11; H, 3.21.

Found: C, 49.08; H, 3.21.

EXAMPLE 111

Preparation of 6-methoxy-2-trifluoromethylbenzamide

A mixture of 6-methoxy-2-trifluoromethylbenzamide (40.0 g, 0.18 mol) in thionyl chloride (50 ml, 0.48 mol) was heated under reflux for three hours. The formed hydrogen chloride was neutralized in an aqueous sodium hydroxide trap. When the evolution of hydrogen chloride stopped, the mixture was cooled to room temperature and the excess thionyl chloride was removed by evaporation under reduced pressure. The resulting acid chloride was added dropwise with vigorous stirring to 250 ml of 12N ammonium hydroxide while cooling to 0° C. in a salt/ice bath. When the addition was complete, the mixture was allowed to warm to ambient temperature and stir for an additional two hours. The solid that formed was collected by filtration, dried under vacuum and recrystallized from methylcyclohexane to give 32.4 g (82 percent of theory) of the title compound as a white solid of m.p. 178°-181° C.

Analysis:

Calculated for $C_9H_8F_3NO_2$: C, 49.31; H, 3.68; N, 6.39.

Found: C, 49.05; H, 3.79; N, 6.34.

EXAMPLE 112

Preparation of 6-methoxy-2-trifluoromethylaniline

Sodium hydroxide (4.6 g, 0.11 mol) was dissolved in 50 ml of water and the solution was cooled to 0° C. in a salt/ice bath. Bromine (5.87 g, 37 mmol) was slowly added to this solution and allowed to stir at 0° C. for 15 minutes. To this rapidly stirred solution was added in portions 6-methoxy-2-trifluoromethylbenzamide (6.4 g, 30.0 mmol) keeping the temperature below 5° C. The mixture was stirred at 0° C. for three hours and then heated to reflux for two hours. It was then allowed to cool to ambient temperature and was extracted with methylene chloride (2×100 ml). The organic phase was combined and dried over magnesium sulfate. The solvent was removed under reduced pressure and the resulting amber liquid distilled to give 4.1 g (71 percent of theory) of the title compound as a clear, colorless oil, b.p. 56° C. at 0.7 mm Hg.

Analysis:

Calculated for $C_8H_8F_3NO$: C, 50,28; H, 4.22; N, 7.33.

Found: C, 50.24; H, 4.12; N, 7.03.

EXAMPLE 113

Preparation of 6-fluoro-2-trifluoromethylbenzoic acid

A mixture of 3-fluorobenzotrifluoride (25.0 g, 0.15 mol) in tetrahydrofuran (200 ml) was cooled to −78° C. in a dry ice/acetone bath under nitrogen atmosphere. To this solution was added dropwise with rapid stirring N-butyl lithium (1.6M, 95.2 ml) at such rate that the temperature did not exceed −60° C. When the addition was complete, the mixture was allowed to stir at −78° C. for an additional five hours. The mixture was then poured over a slurry of dry ice/ether and allowed to come to room temperature. The solvent was removed by evaporation under reduced pressure to obtain a white solid residue. This solid was dissolved in a minimum amount of water, the solution was extracted with diethyl ether (2×100 ml) and the aqueous phase was acidified to pH 2 with dilute hydrochloric acid. An oil formed and this was dissolved in diethyl ether; the solution was washed several times with water and dried over magnesium sulfate. The solvent was removed by evaporation under reduced pressure to give a white solid. NMR analysis indicated this product was a mixture of the title compound and an isomer. A yield of 15.6 g (50 percent of theory) was obtained.

Analysis:

Calculated for $C_8H_4F_4O_2$: C, 46.17; H, 1.94.

Found: C, 46.29; H, 1.73.

EXAMPLE 114

Preparation of 6-fluoro-2-trifluoromethylbenzamide

A mixture of 6-fluoro-2-trifluoromethylbenzoic acid and its isomer (19.6 g, 0.10 mol) and thionyl chloride (35 ml) was heated under reflux for two hours. The hydrogen chloride formed was neutralized in an aqueous sodium hydroxide trap. When the evolution of hydrogen chloride stopped, the mixture was cooled to room temperature and the excess thionyl chloride was removed by evaporation under reduced pressure. This was added dropwise with vigorous stirring to 250 ml of 12N ammonium hydroxide while cooling to 0° C. in a salt/ice bath. When the addition was complete the mixture was allowed to warm to ambient temperature and stir for an additional two hours. The solid that formed was collected by filtration, dried under vacuum, and recrystallized from hexane to give two products. The first precipitated from hexane at room temperature to give 14.2 g of the desired 6-fluoro-2-trifluoromethylbenzamide which melts at 165°-6° C. and the remainder precipitated when the hexane was removed under reduced pressure to give 4.5 g of the 2-fluoro-4-trifluoromethylbenzamide, which melts at 143°-4° C. The total yield was 18.7 g which is 84 percent of theory.

Analysis:

Calculated for $C_8H_5F_4NO_2$: C, 43.06; H, 2.26; N, 6.28.

Found: C, 43.41; H, 2.13; N, 6.07.

EXAMPLE 115

Preparation of 2,6-difluoro-3-methylaniline

Sodium hydroxide (5.6 g, 0.14 mol) was dissolved in 50 ml of water and then cooled to 0° C. in a salt/ice bath. Bromine (9.60 g, 60.0 mmoles) was slowly added to this solution and allowed to stir at 0° C. for 15 minutes. To this solution was added in portions with rapid stirring 2,6-difluoro-3-methylbenzamide (7.0 g, 37.0 mmol) keeping the temperature below 5° C. The mixture was stirred at 0° C. for three hours and then heated to reflux for two hours. It was then allowed to cool to ambient temperature and was extracted with methylene chloride (2×100 ml). The organic phases were combined and dried over magnesium sulfate. The solvent was removed by evaporation under reduced pressure and the resulting amber liquid distilled to give the title compound a clear, colorless oil having a b.p. of 107° C. at 15 mm Hg and amounting to 2.1 g (36 percent of theory).

Analysis:

Calculated for $C_7H_7F_2NO$: C, 52.84; H, 4.43; N, 8.80

Found: C, 52.59; H, 4.73; N, 8.97

EXAMPLE 116

Preparation of 6-trifluoromethoxy-2-trifluoromethylaniline

Sodium hydroxide (20.0 g, 0.50 mole) was dissolved in 150 ml of water and the solution cooled to 0° C. in a salt/ice bath. Bromine (11.3 g, 70.7 mmoles) was slowly added to this solution and allowed to stir at 0° C. for 15 minutes. To this solution was added in portions with rapid stirring 6-trifluoromethoxy-2-trifluoromethylbenzamide (7.0 g, 37.0 mmoles) keeping the temperature below 5° C. The mixture was stirred at 0° C. for five hours and then heated to reflux for 18 hours. It was then allowed to cool to ambient temperature and was extracted with ether (2×100 ml). The organic phases were combined and dried over magnesium sulfate. The solvent was removed by evaporation under reduced pressure and the resulting amber liquid distilled to give the title compound a clear, colorless oil having a b.p. of 152°-153° C. at 760 mm Hg and amounting to 8.2 g (47 percent of theory).

Analysis:
Calculated for $C_8H_5F_6NO$: C, 39.20; H, 2.06; N, 5.72;
Found: C, 38.76; H, 1.99; N, 5.69

EXAMPLE 117

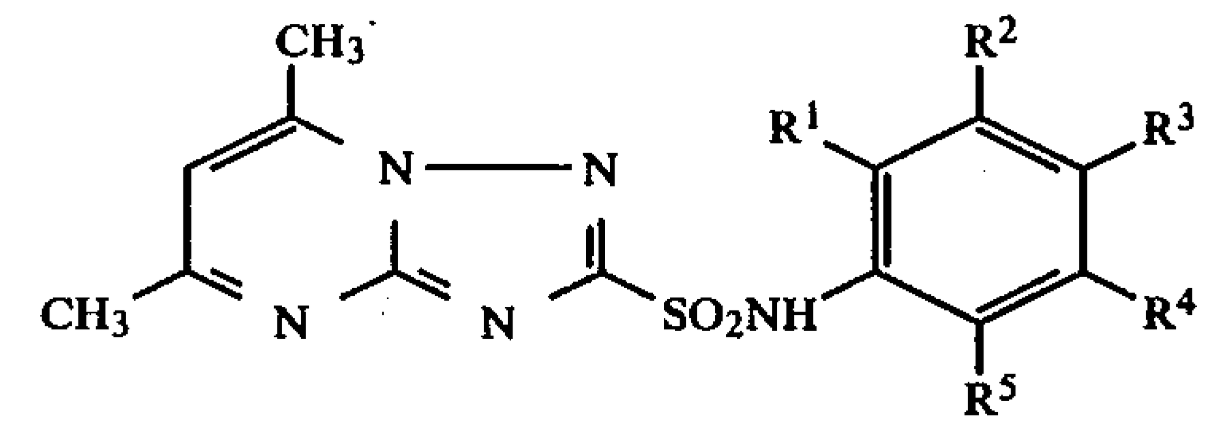
Preparation of 2-fluoro-6-methylthioaniline

A mixture of N-(t-butoxycarbonyl)-2-fluoroaniline (5.0 g, 24 mmoles) in anhydrous tetrahydrofuran (50 ml) was cooled to −78° C. under a nitrogen atmosphere. To this solution was added t-butyl lithium (2.0M, 57.6 mmoles, 28.8 ml) at such a rate that the temperature did not exceed −65° C. When the addition was complete, the mixture was stirred at −78° C. for an additional 15 minutes and at −20° C. for 2.5 hours. To this reaction mixture was added dimethyl disulfide (2.82 g, 30 mmoles) in 10 ml of anhydrous tetrahydrofuran while maintaining the temperature at −20° C. for an additional hour. The mixture was allowed to warm to ambient temperature and then 25 ml of 1N sodium hydroxide was added. The mixture obtained was extracted with diethyl ether (2×100 ml). The organic phase was separated and dried over magnesium sulfate and then the solvent was removed by evaporation under reduced pressure to obtain a tan solid. This was hydrolized in dilute hydrochloric acid (6N, 200 ml) by heating to reflux for three hours. The resulting solution was extracted with diethyl ether and the aqueous layer was neutralized with sodium hydroxide (6N, 200 ml), and extracted with methylene chloride, dried over magnesium sulfate and the solvent removed by evaporation under reduced pressure to obtain an amber oil. This was distilled to give 3.2 g (85% of theory) of the title compound, having a b.p. of 62°-65° C. at 0.2 mm Hg.

Analysis:
Calculated for C_7H_8FNS: C, 58.48; H, 5.13; N, 8.91.
Found: C, 53.84; H, 5.55; N, 8.73.

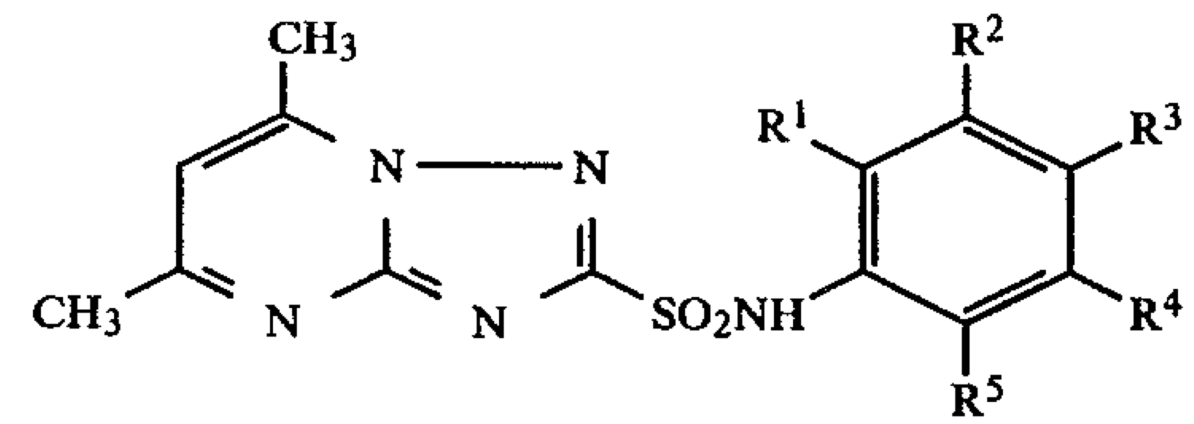
Representative compounds prepared employing the above general procedures are tabulated in the following Tables I through LII.

TABLE I



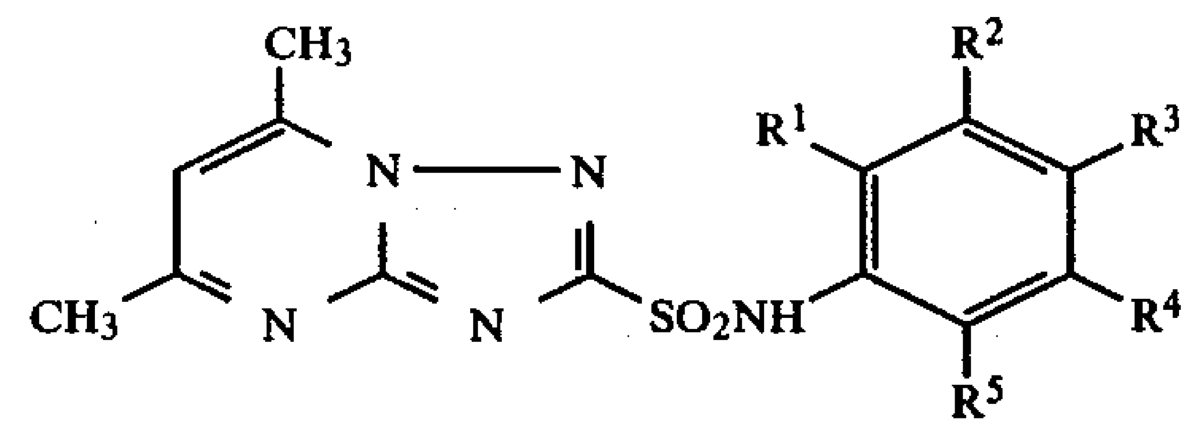
Compound	R^1	R^2	R^3	R^4	R^5	Melting Point	Elemental Analysis					
							Analysis	C	H	N	Cl	S
1	CF_3	H	H	H	OCH_2CF_3	247–249° C.	Calcd. for $C_{16}H_{13}F_6N_5O_2S$:	40.9	2.79	14.92		
							Found:	39.9	2.78	14.75		
2	CH_3	H	H	H	H	222–224° C.	Calcd. for $C_{14}H_{15}N_5O_2S$:	52.99	4.76	22.06		
							Found:	52.75	4.79	22.25		
3	OH	H	H	H	H	>150° C. (decomp.)	Calcd. for $C_{13}H_{13}N_5O_3S$:	48.90	4.10	21.92		
							Found:	48.45	4.15	21.77		
4	OCH_3	H	H	H	H	208°–210.5° C.	Calcd. for $C_{14}H_{15}N_5O_3S$:	50.44	5.54	21.00		
							Found:	50.17	4.54	21.12		
5	$NHCH_3$	H	H	H	H	227°–228° C.	Calcd. for $C_{14}H_{16}N_6O_2S$:	50.59	4.85	25.28		
							Found:	49.70	4.87	25.12		
6	I	H	H	H	H	189°–192° C.	Calcd. for $C_{13}H_{12}IN_5O_2S$:	36.38	2.82	16.31		
							Found:	36.61	2.81	16.15		
7	Cl	H	H	H	H	188°–189.5° C.	Calcd. for $C_{13}H_{12}ClN_5O_2S$:	46.23	3.58	20.73	10.50	9.49
							Found:	46.09	3.58	20.89	10.34	9.37
8	—F	H	H	H	H	189°–190° C.	Calcd. for $C_{13}H_{12}FN_5O_2S$:	48.59	3.76	21.79	9.98	
							Found:	48.79	3.74	21.88	9.86	
9	SCH_3	H	H	H	H	142°–144° C.	Calcd. for $C_{14}H_{15}N_5O_2S_2$:	48.13	4.33	20.04		
							Found	47.99	4.28	20.40		
10	$COOCH_3$	H	H	H	H	169.5–170° C.	Calcd. for $C_{15}H_{15}N_5O_4S$:	49.86	4.18	19.38	8.87	
							Found: 49.68	4.13	19.35	8.69		
11	COOH	H	H	H	H	247°–248° C.	Calcd. for $C_{14}H_{13}N_5O_4S$:	48.41	3.77	20.16	9.23	
							Found:	47.87	3.66	20.27	8.87	
12	NO_2	H	H	H	H	140° C.	Calcd. for $C_{13}H_{12}N_6O_4S$:	44.83	3.47	24.13	9.21	
							Found:	44.91	3.48	24.11	9.11	
13	CF_3	H	H	H	H	198.5–200.5° C.	Calcd. for $C_{14}H_{12}F_3N_5O_2S$:	45.28	3.26	18.86	8.63	
							Found:	45.39	3.16	18.74	8.87	
14	—CN	H	H	H	H	237.5–239° C.	Exact mass calcd for $C_{14}H_{12}N_6O_2S$:			328.0742		
							Found:			328.0748		
							Analysis	C	H	N	Cl	S
15	$—SO_2nMe_2$	H	H	H	H	91° C.	Calcd. for $C_{15}H_{18}N_6O_4S_2$:	43.89	4.42	20.47	15.62	
							44.25	4.37	20.21	15.23		
16	$—SO_2N(Me)Et$	H	H	H	H	80° C.	Calcd. for $C_{16}H_{20}N_6O_4S_2$:	45.27	4.75	19.80	15.11	
							Found:	45.07	4.64	19.60	14.77	
17	H	—Cl	H	H	H	231°–232.5° C.	Exact mass calcd. for $C_{13}H_{12}ClN_5O_2S$:			337.0400		
							Found:			337.0415		
18	H	H	—Cl	H	H	237°–239° C.	Exact mass calcd. for $C_{13}H_{12}ClN_5O_2S$:			337.0400		
							Found:			337.0411		
							Analysis	C	H	N	Cl	S
19	Cl	Cl	H	H	H	214.5–216.5° C.	Calcd. for $C_{13}H_{11}Cl_2N_5O_2S$:	41.95	2.98	18.81	19.05	8.61
							Found:	42.02	3.03	18.99	18.24	8.30

TABLE I-continued



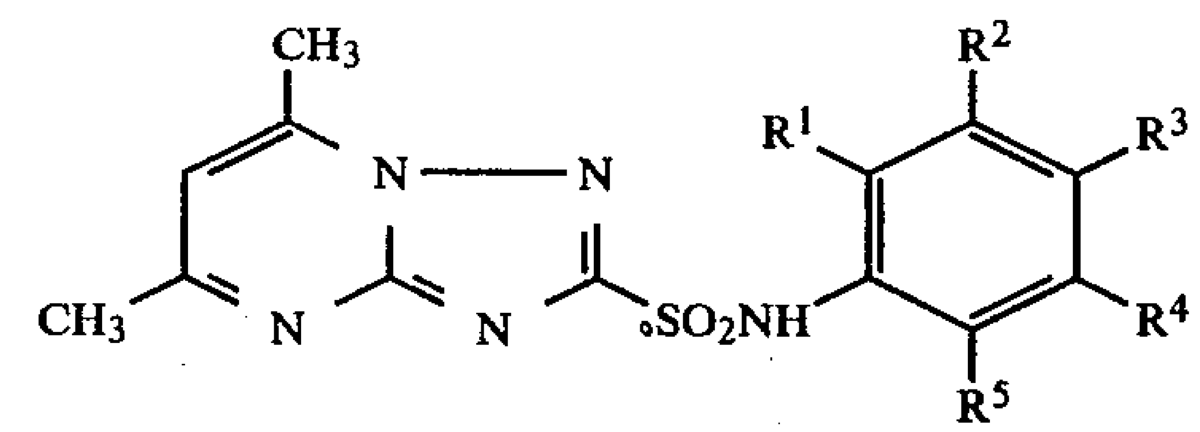
Compound	R^1	R^2	R^3	R^4	R^5	Melting Point	Elemental Analysis					
20	Cl	H	Cl	H	H	176°-177.5° C.	Calcd. for $C_{13}H_{11}Cl_2N_5O_2S$:	41.95	2.98	18.81	19.05	8.61
							Found:	42.24	2.94	18.90	18.83	8.82
21	Cl	H	H	Cl	H	250°-253° C.	Exact mass calcd. for $C_{13}H_{11}Cl_2N_5O_2S$:			371.0010		
							Found:			370.9997		
							Analysis	C	H	N	Cl	S
22	Cl	H	H	H	Cl	260.5-262.5° C.	Calcd. for $C_{13}H_{11}Cl_2N_5O_2S$:	41.95	2.98	18.81	19.05	8.61
							Found:	42.12	2.94	19.01	18.89	8.57
23	H	Cl	Cl	H	H	240°-242° C.	Calcd. for $C_{13}H_{11}Cl_2N_5O_2S$:	41.95	2.98	18.81	19.05	8.61
							Found:	42.32	2.87	18.82	18.65	8.42
24	H	Cl	H	Cl	H	273.5-275.5° C.	Calcd. for $C_{13}H_{11}Cl_2N_{N5}O_2S$:	41.95	2.98	18.81	19.05	8.61
							Found:	42.30	2.89	18.42	18.85	8.49
25	F	H	H	H	F	229.5-231° C.	Exact mass calcd. for $C_{13}H_{11}F_2N_5O_2S$:			3339.0630		
							Found:			339.0602		
							Analysis	C	H	N	Cl	S
26	COOMe	H	H	H	F	181.5-183.5° C.	Calcd. for $C_{15}H_{14}Fn_5O_4S$: 47.49	3.72	18.46	8.45		
							Found:	47.65	3.60	18.19	8.35	
27	COOH	H	H	H	F	228.5-230° C.	Calcd. for $C_{14}H_{12}FN_5O_4S$:	46.03	3.31	19.17	8.78	
							Found:	45.56	3.26	19.05	8.50	
28	SO_2NMe_2	H	H	CF_3	H	174.5-176.5° C.	Calcd. for $C_{16}H_{17}F_3N_6O_4S_2$:	40.16	3.58	17.56	13.40	
							Found:	40.16	3.49	17.39	13.17	
29	F	H	F	H	H	233°-224.5° C.	Calcd. for $C_{13}H_{11}F_2N_5O_2S$:	46.02	3.27	20.63		
							Found:	46.19	3.37	20.59		
30	Cl	H	F	H	H	203°-205° C.	Calcd. for $C_{13pl\ H11}ClFN_5O_2S$:	43.89	3.12	19.68		
							Found:	44.02	3.12	19.89		
31	Cl	H	H	H	CH_3	230°-231.5° C. (decomp.)	Calcd. for $C_{14}H_{14}ClN_5O_2S$:	47.82	3.98	19.07		
							Found:	47.87	4.06	19.66		
32	Ch_3	H	H	H	CH_3	263°-266° C. (decomp.)	Calcd. for $C_{15}H_{17}N_5O_2S$:	54.31	5.23	21.23		
							Found:	53.59	5.07	20.65		
33	CH_2CH_3	H	H	H	CH_2CH_3	248-249.5° C. (decomp.)	Calcd. for $C_{17}H_{21}N_5N_5O_2S$:	56.83	5.84	19.48		
							Found:	57.06	5.98	19.40		
34	—CF_3	H	—Cl	H	H	189°-193° C. (decomp.)	Calcd. for $C_{14}H_{11}ClF_3N_5O_2S$:	41.41	2.71	17.25		
							Found:	41.78	2.73	17.23		
35	—Cl	H	—Cl	H	—Cl	>200° C. (decomp.)	Calcd. for $C_{13}H_{10}Cl_3N_5O_2S$:	38.40	2.48	17.22		
							Found:	38.36	2.48	17.14		
36	—COOiPr	H	H	H	H	130°-132° C.	Calcd. for $C_{17}H_{19}N_5O_4S$:	52.43	4.92	17.98		
							Found:	51.83	4.77	17.70		
37	—$CONH_2$	H	H	H	H	258°-260° C.	Calcd. for $C_{14}H_{14}N_6O_3S$:	48.55	4.07	24.26		
							Found:	48.58	4.00	24.01		
38	—Br	H	H	H	—Br	285°-287° C.	Calcd. for $C_{13}H_{11}Br_2N_5O_2S$:	33.86	2.40	15.18		
							Found:	33.92	2.42	15.41		
39	—Br	H	H	H	—Cl	>230° C. (decomp.)	Calcd. for $C_{13}H_{11}BrClN_5O_2S$::	37.47	2.66	16.80		
							Found:	37.50	2.64	16.87		

TABLE I-continued



Compound	R¹	R²	R³	R⁴	R⁵	Melting Point	Elemental Analysis	C	H	N	Cl	S
40	—Br	H	—Cl	H	H	177°-179° C.	Calcd. for $C_{13}H_{11}BrClN_5O_2S$:	37.47	2.66	16.80		
							Found:	37.45	2.67	16.64		
41	—Br	H	H	H	H	188°-190° C.	Calcd. for $C_{13}H_{12}BrN_5O_2S$:	40.85	3.16	18.32		
							Found:	41.09	3.12	18.19		
42	—CONMe₂	H	H	H	H	193°-194° C.	Calcd. for $C_{16}H_{18}N_6O_3S$:	51.33	4.85	22.44		
							Found:	51.08	4.65	22.12		
43	—CONMe₂	H	—Cl	H	H	194°-195°C.	Calcd. for $C_{16}H_{17}ClN_6O_3S$:	47.00	4.19	20.55		
							Found:	47.16	4.07	20.50		
44	—Cl	H	F	H	—Cl	271°-273° C.	Calcd. for $C_{13}H_{10}Cl_2FN_5O_2S$:	40.02	2.58	17.94		
						(decomp.)	Found:	40.13	2.65	18.04		
45	—SO₂Me	H	H	H	H	181°-183° C.	Calcd. for $C_{14}H_{15}N_5O_4S_2$:	44.09	3.96	18.35		
							Found:	43.64	3.84	18.16		
46	—Cl	—Me	H	H	—Cl	280° C.	Calcd. for $C_{14}H_{13}Cl_2N_5O_2S$:	43.54	3.39	18.13		
						(decomp.)	Found:	43.45	3.37	18.15		
47	—Cl	H	—Me	H	—Cl	245°-248° C.	Calcd. for $C_{14}H_{13}Cl_2N_5O_2S$:	43.54	3.39	18.13		
							Found:	43.57	3.37	18.21		
48	—Cl	H	—Me	H	H	229°-231° C.	Calcd. for $C_{14}H_{14}ClN_5O_2S$:	48.00	4.01	19.90		
							Found:	48.01	3.97	20.05		
49	—NO₂	H	H	H	—CH₃	244°-246° C.	Exact mass calcd. for $C_{14}H_{14}N_6O_4S$:			362.0799		
							Found:			362.0807		
							Analysis	C	H	N	Cl	S
50	—COOMe	H	H	H	—CH₃	CAlcd. for $C_{16}H_{17}N_5O_4S$:	51.19	4.57	18.65			
							Found:	51.22	4.58	18.46		
51	—COOi-Pr	H	H	H	F	167°-168° C.	Calcd. for $C_{17}H_{18}FN_5O_4S$:	50.12	4.45	17.18		
							Found:	50.09	4.39	17.28		
52	—I	H	H	—CF₃	H	221.5°-224° C.	Calcd. for $C_{14}H_{10}ClF_3N_5O_2S$:	41.43	2.71	17.24		
							Found:	41.73	2.74	17.08		
53	—I	H	H	H	—Cl	>258° C.	Calcd. for $C_{13}H_{11}ClIN_5O_2S$:	33/68	2.39	15.10		
						(decomp.)	Found:	33.66	2.38	15.03		
54*	—Cl	H	H	H	—F	223°-225.5° C.	Calcd. for $C_{13}H_{11}ClFN_5O_2S$:	43.89	3.12	19.68		
						(decomp.)	Found:	43.20	2.89	19.41		
55	SCF₃	H	H	H	H	175-178° C.	Calcd. for $C_{14}H_{12}F_3N_5O_2S_2$:	41.68	2.97	17.35		
							Found:	40.84	2.95	16.61		
56	COO—t-Bu	H	H	H	F	151-153° C.	Cald. for $C_{18}H_{20}FN_5O_4S$:	51.30	4.78	16.61		
						(decomp.)	Found:	50.90	4.69	16.49		
57	SO₂CF₃	H	H	H	H	68-70° C.	Calcd. for $C_{14}H_{12}F_3N_5O_4S_2$:	38.62	2.75	16.09		
							Found:	39.10	2.71	15.87		
58	Br	H	H	H	CH₃	225-228° C.	Calcd. for $C_{14}H_{14}BrN_5O_2S$:	42.44	3.56	17.67		
							Found:	42.56	3.55	17.66		
59	SCF₂CF₂H	H	H	H	H	162.5-164° C.	Calcd. for $C_{15}H_{13}F_4N_5O_2S_2$:	41.38	3.01	16.08	14.73	
							Found:	41.54	2.88	16.06	14.57	

TABLE I-continued



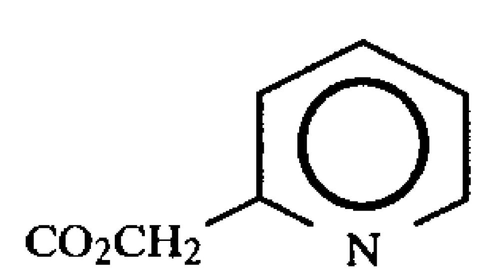
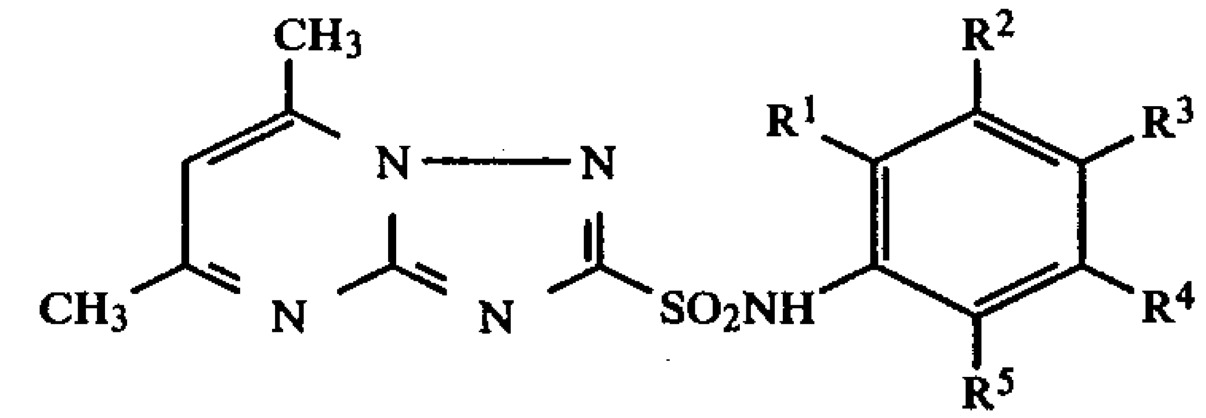
Compound	R^1	R^2	R^3	R^4	R^5	Melting Point	Elemental Analysis				
60	$SOCF_2CF_2H$	H	H	H	H	223–224° C.	Calcd. for $C_{15}H_{13}F_4N_5O_3S_2$:	39.91	2.90	15.51	14.21
							Found:	39.88	2.83	15.37	14.15
61	$CONH_2$	H	H	H	CH_3	231–232° C.	Calcd. for $C_{15}N_{16}N_6O_3S$. H_2O:	47.61	4.80	22.20	
							Found:	47.74	4.71	22.04	
62	$CONMe_2$	H	H	H	CH_3	225–257° C.	Calcd: for $C_{17-16N6}O_3S$:	52.57	5.19	21.63	
							Found:	52.19	5.15	21.39	
63	Cl	H	H	H	Ph	256–260° C. (decomp.)	Calcd. for $C_{19}H_{16}ClN_5O_2S$:	55.14	3.90	16.92	
							Found:	54.68	3.89	16.96	
64	Coo—i-Pr	H	H	H	CH_3	178–179° C.	Calcd. for $C_{18}H_{21}N_5O_4S$:	53.59	5.25	17.35	
							Found:	53.32	5.18	17.15	
65	CH_3	Cl	H	H	CH_3	279–282° C. (decomp.)	Calcd. for $C_{15}H_{16}C'N_5O_2S$:	49.25	4.41	19.14	
							Found:	49.05	4.38	19.00	
66	$SCH_2CH{=}CH_2$	H	H	H	H	113–114° C.	Calcd. for $C_{16}H_{17}N_5O_2S_2$:	51.17	4.56	18.65	
							Found:	51.29	4.63	18.94	
67	$SCH_2CH_2CH_3$	H	H	H	H	124° (decomp.)	Calcd. for $C_{16}H_{19}N_5O_2S_2$:	50.90	5.07	18.55	
							Found:	50.41	4.76	18.79	
68	CH_3	Cl	H	H	H	223–225° C.	Calcd. for $C_{14}H_{14}ClN_5O_2S$:	47.79	4.01	19.91	
							Found:	47.52	4.31	19.84	
69	SCH_3	H	H	H	Cl	171–172° C	Calcd. for $C_{14}H_{14}ClN_5O_2S_2$:	43.80	3.68	18.24	
							Found:	44.00	3.74	17.96	
70	SCH_3	H	H	H	CH_3	200–202° C.	Calcd. for $C_{15}H_{17}N_5O_2S_2$:	49.56	4.71	19.27	
							Found:	49.78	4.49	18.68	
71	$CH{=}NOH$	H	H	H	OCH_3	244–246° C.	Calcd. for $C_{15}H_{16}N_6O_4S$:	47.86	4.29	22.33	
							Found:	47.47	4.03	23.36	
72	$CO_2CH_2CH_2OEt$	H	H	H	CH_3	78–80° C.	Calcd. for $C_{19}H_{23}N_5O_5S$:	52.65	5.35	16.16	
							Found:	51.68	5.11	16.37	
73	$CO_2CH_2CH_2NMe_2$	H	H	H	CH_3	207–208° C.	Calcd. for $C_{19}H_{24}N_6O_4S$:	52.76	5.59	19.43	
							Found:	52.06	5.48	19.18	
74	Cl	Cl	H	H	CH_3	287–289° C. (decomp.)	Calcd. for $C_{14}H_{13}Cl_2N_5O_2S$:	43.54	3.39	18.13	
							Found:	43.74	3.46	18.48	
75	COOPh	H	H	H	CH_3	159.5–160.5° C.	Calcd. for $C_{21}H_{19}N_5O_4S$:	57.66	4.38	16.01	
							Found:	57.17	4.46	15.74	
76	$CO_2CH_2CH{=}CH_2$	H	H	H	CH_3	158–158.5° C.	Calcd. for $C_{18}H_{19}N_5O_4S$:	53.86	4.77	17.44	
							Found:	53.47	4.63	17.54	
77		H	H	H	CH_3	165.5–166° C	Calcd. for $C_{21}H_{20}N_6O_4S$:	55.74	4.46	18.57	
							Found:	55.82	4.43	18.32	
78	$CO_2N{=}C(CH_3)_2)$	H	H	H	CH_3	91–94° C.	Calcd. for $C_{18}H_{20}N_6O_4S$:	51.91	4.84	10.18	
							Found:	51.51	4.68	19.70	

TABLE I-continued



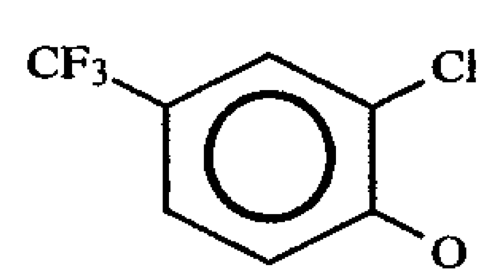
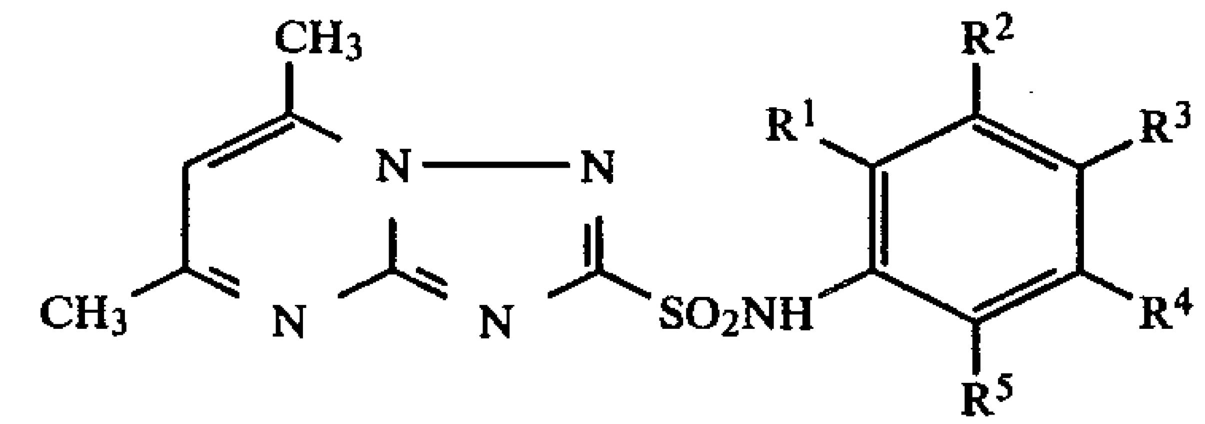
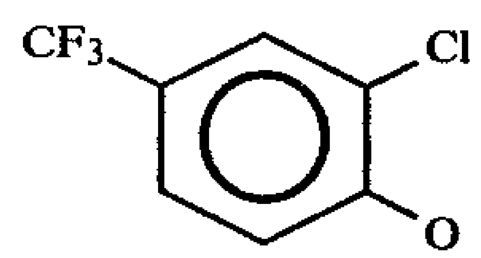
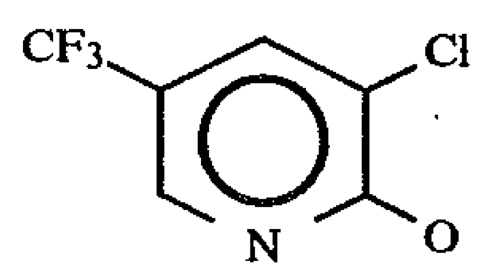
Compound	R1	R2	R3	R4	R5	Melting Point	Elemental Analysis			
79	CH=N—OCH3	H	H	H	OCH3	227–229° C.	Calcd. for $C_{16}H_{18}N_6O_4S$:	49.22	4.65	21.53
							Found:	49.00	4.63	21.24
80	S—t-Bu	H	H	H	H	144–146° C.	Calcd. for $C_{17}H_{21}N_5O_2S_2$:	52.15	5.41	17.89
							Found:	52.31	5.34	17.92
81	Cl	H	H	COOMe	H	175–177° C.	Calcd. for $C_{15}H_{14}ClN_5O_4S$:	45.52	3.57	17.69
							Found:	45.42	3.45	17.66
82	Cl	COOMe	H	H	Cl	217–221° C.	Calcd. for $C_{15}H_{13}Cl_2N_5O_4S$:	41.87	3.05	16.27
						(decomp.)	Found:	41.96	3.10	16.22
83	Cl	CF3	H	H	Cl	286–290° C.	Calcd. for $C_{14}H_{10}Cl_2F_3N_5O_2S$:	38.20	2.29	15.90
						(decomp.)	Found:	38.36	2.29	16.63
84	Cl	H	H	CO2—i-Pr	H	182–185° C.	Calcd. for $C_{17}H_{18}ClN_5O_4S$:	48.17	4.28	16.52
							Found:	48.31	4.17	16.51
85	NO2	H	H	CH3	CH3	254–257° C.	Calcd. for $C_{15}H_{16}N_6O_4S$:	47.87	4.29	22.32
						(decomp.)	Found:	47.52	4.01	22.47
86	Br	COOMe	H	H	CH3	229–231° C.	Calcd. for $C_{16}H_{16}BrN_5O_4S$:	42.30	3.55	15.41
							Found:	42.29	3.45	15.68
87	Br	COO—i-Pr	H	H	CH3	208–211° C.	Calcd. for $C_{18}H_{20}BrN_5O_4S$:	44.82	4.18	14.51
							Found:	45.09	4.11	14.39
88	Br	COO—t-Bu	H	H	CH3	181–183° C.	Calcd. for $C_{19}H_{22}BrN_5O_4S$:	45.98	4.47	14.10
						(decomp.)	Found:	45.61	4.17	13.84
89	COMe	H	H	H	H	166–168° C.	Calcd. for $C_{15}H_{15}N_5O_3S$:	52.16	4.38	20.28
							Found:	52.07	4.19	20.37
90	F	F	H	F	F	148–149° C.	Calcd. for $C_{13}H_9F_4N_5O_2S$:	41.60	2.42	18.66
						(decomp.)	Found:	42.25	2.50	18.52
91	CH2OCH3	H	H	H	Cl	201–202° C.	Calcd. for $C_{15}H_{16}ClN_5O_3S$:	47.19	4.22	18.33
							Found:	47.07	4.16	18.87
92	CH2OCH2Ph	H	H	H	Cl	169–171° C.	Calcd. for $c_{21}H_{20}cLN_5O_3S$:	55.08	4.40	15.29
							Found:	54.99	4.38	15.30
93	CH2OH	H	H	H	Cl	208–209° C.	Calcd. for $C_{14}H_{14}ClN_5O_3S.H_2O$:	43.60	4.18	18.14
							Found:	43.50	3.75	18.43
94	CH2OAc	H	H	H	Cl	214–217° C.	Calcd. for $C_{16}H_{16}ClN_5O_4S$:	46.89	3.94	17.08
							Found:	46.60	3.80	17.73
95	COPh	H	H	H	H	169–170° C.	Calcd. for $C_{20}H_{17}N_5O_3S$:	58.95	4.21	17.19
							Found:	58.67	4.14	17.51
96	SO2Ph	H	H	H	H	152–154° C.	Calcd. for $C_{19}H_{17}N_5O_4S_2$:	51.46	3.86	15.79
							Found:	51.31	3.81	15.81
97		H	H	H	H	176–177° C.	Calcd. for $C_{20}H_{15}ClF_3N_5O_3S$:	48.24	3.03	14.06
							Found:	48.11	3.09	14.49

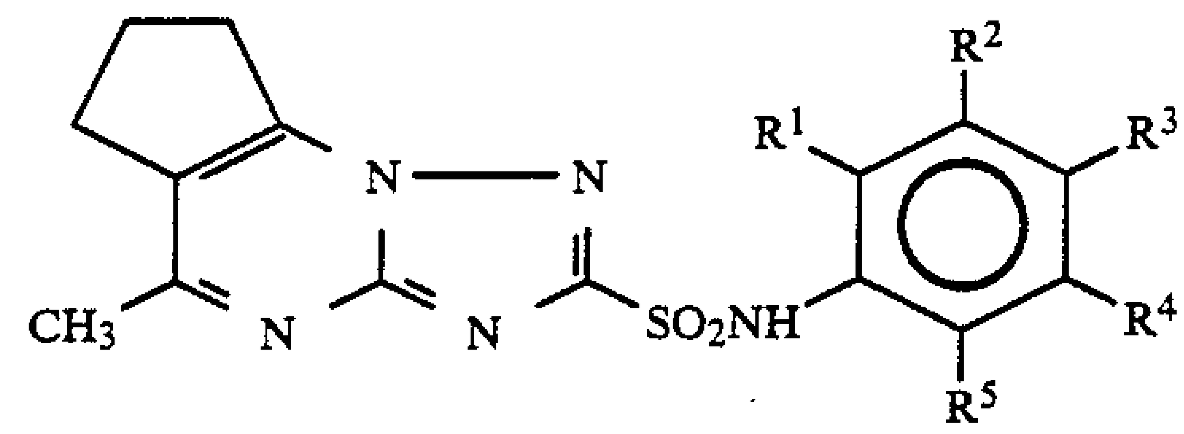
TABLE I-continued



Compound	R^1	R^2	R^3	R^4	R^5	Melting Point	Elemental Analysis			
98		H	H	H	F	211–213° C.	Calcd. for $C_{20}H_{14}ClF_4N_5O_3S$:	46.56	2.74	13.57
							Found:	46.02	2.74	13.40
99		H	H	H	H	178–180° C.	Calcd. for $C_{19}H_{14}ClF_3N_6O_3S$:	45.74	2.84	16.85
							Found:	45.66	2.81	17.02
100	Cl	H	H	COOH	H	276–278° C.	Calcd. for $C_{14}H_{12}ClN_5O_4S$:	44.04	3.17	18.34
							Found:	44.06	3.24	18.37
101	Br	COOH	H	H	CH_3	290° C.	Calcd. for $C_{15}H_{14}BrN_5O_4S$:	40.92	3.21	15.90
						(decomp.)	Found:	40.51	3.11	16.01
102	CO_2Me	H	H	CO_2Me	H	191–194° C.	Calcd. for $C_{17}H_{17}N_5O_6S$:	48.68	4.09	16.70
							Found:	48.47	4.01	16.32
103	COOH	H	H	H	CH_3	268–271° C.	Calcd. for $C_{15}H_{15}N_5O_4S.\frac{1}{2}H_2O$:	48.64	4.35	18.90
							Found:	48.88	4.00	19.20
104	CF_3	H	H	H	OCH_3	246–249° C.	Calcd. for $C_{15}H_{14}F_3N_5O_3S$:	44.91	3.49	17.47
							Found:	44.77	3.61	17.94

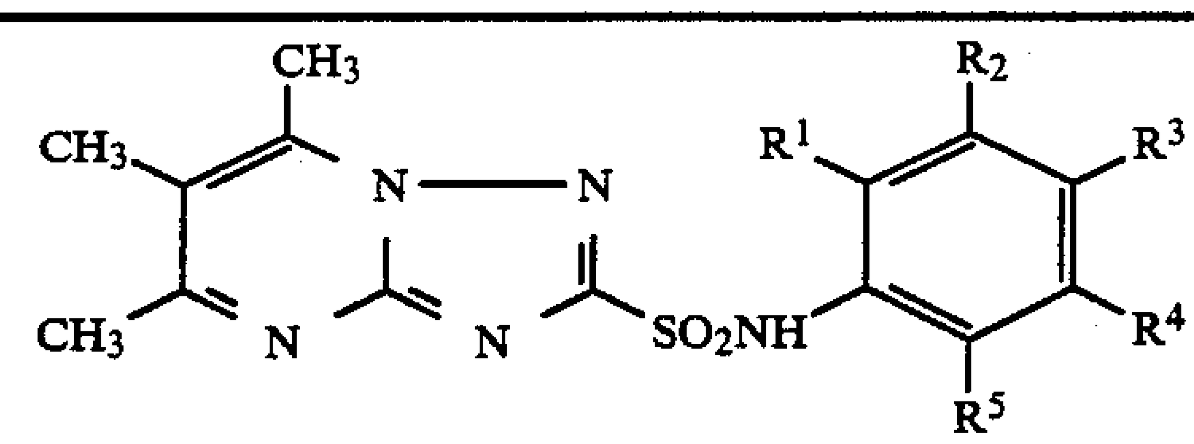
*This compound contains 15% where $R^1 = R^3 = Cl$ and $R^5 = F$.

TABLE II



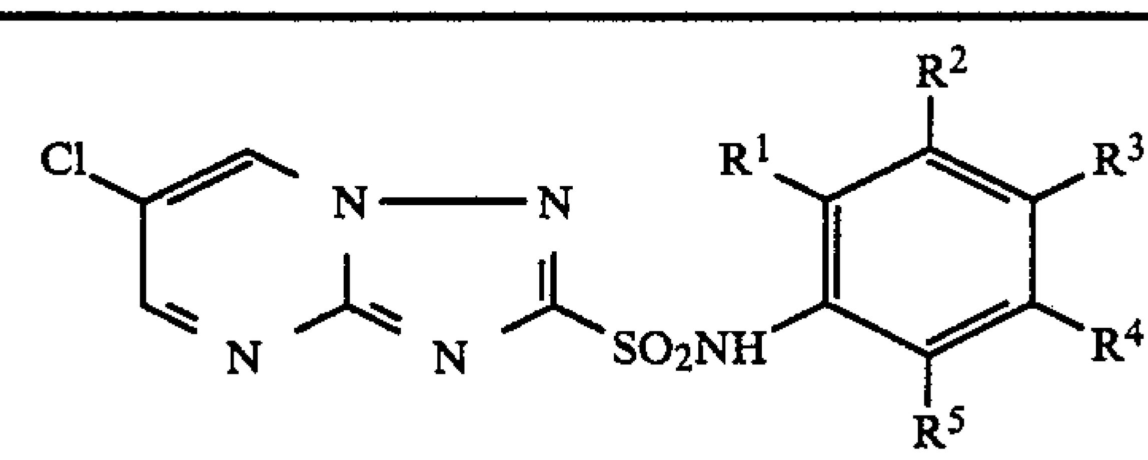
Compound	R[1]	R[2]	R[3]	R[4]	R[5]	Melting Point	Elemental Analysis: Analysis	C	H	N
105	NO_2	H	H	H	H	110°-112° C. (decomp.)	Calcd. for $C_{15}H_{14}N_6O_4S$:	48.11	3.73	22.43
							Found:	46.96	3.54	21.62
106	CF_3	H	H	H	H	ca. 200° C.	Calcd. for $C_{16}H_{14}F_3N_5O_2S$:	48.35	3.52	17.61
							Found:	48.08	3.40	17.40
107	SO_2NMe_2	H	H	H	H	188°-189° C. (decomp.)	Calcd. for $C_{17}H_{20}N_6O_4S_2$:	46.78	4.58	19.24
							Found:	46.04	4.85	18.90
108	Cl	H	H	H	H	264°-266° C.	Calcd. for $C_{15}H_{13}Cl_2N_5O_2S$:	45.24	3.29	17.58
							Found:	45.47	3.18	17.41
109	—COOMe	H	H	H	H	180°-182° C. (decomp.)	Calcd. for $C_{17}H_{17}N_5O_4S$:	52.71	4.42	18.07
							Found:	52.19	4.28	18.12
110	—COO—i-Pr	H	H	H	H	170°-172° C.	Calcd. for $C_{19}H_{21}N_5O_4S$:	54.93	5.10	16.85
							Found:	54.82	5.01	16.59

TABLE III



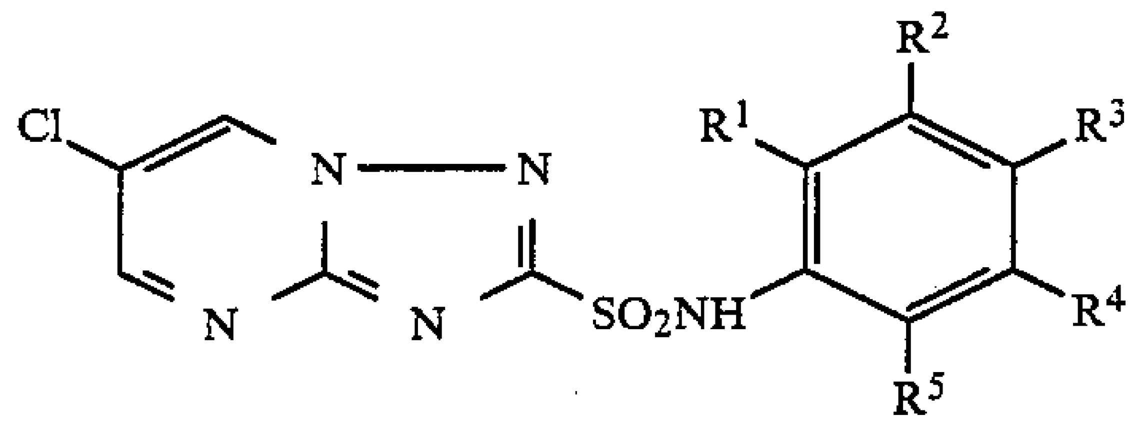
Cmpd.	R[1]	R[2]	R[3]	R[4]	R[5]	Melting Point	Elemental Analysis: Analysis	C	H	N	S	Cl
111	Cl	H	H	H	Cl	296-298° C.	Calcd. for $C_{14}H_{13}Cl_2N_5O_2S$:	43.53	3.39	18.13	8.30	18.36
							Found:	44.07	3.42	18.16	7.89	17.73
112	CF_3	H	H	H	H	197-199° C.	Calcd. for $C_{15}H_{14}F_3N_5O_2S$:	46.75	3.66	18.17	8.32	
							Found:	46.54	3.52	18.30	8.59	
113	Cl	H	H	H	CH_3	306-309° C.	Calcd. for $C_{15}H_{16}ClN_5O_2S$:	49.25	4.41	19.14	8.76	9.69
							Found:	48.70	4.29	19.23	8.82	9.57

TABLE IV



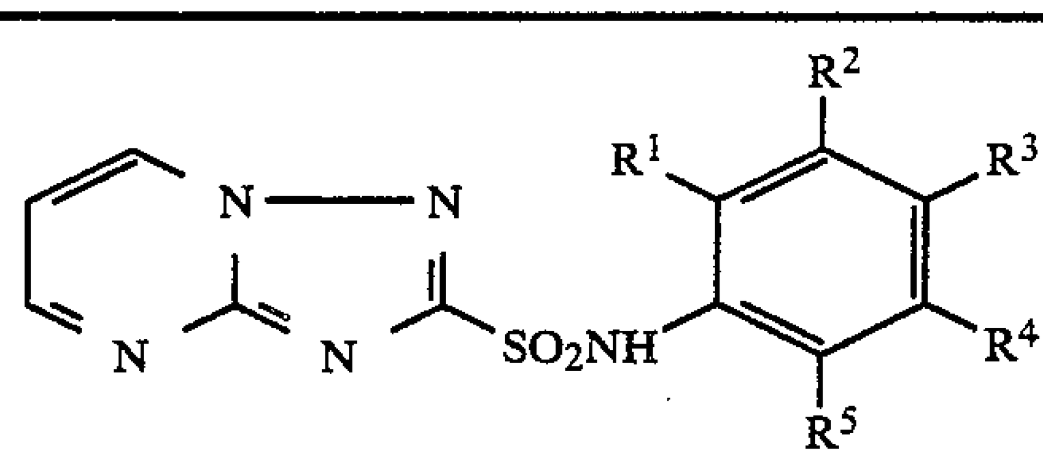
Cmpd.	R[1]	R[2]	R[3]	R[4]	R[5]	Melting Point	Elemental Analysis: Analysis	C	H	N
114	—Cl	H	H	H	—Cl	246-248° C.	Calcd. for $C_{11}H_6Cl_3N_5O_2S$:	34.89	1.60	18.50
							Found:	35.02	1.65	18.09
115	—SMe	H	H	H	H	159-162° C.	Calcd. for $C_{12}H_{10}ClN_5O_2S_2$:	40.50	2.81	19.60
							Found:	40.39	2.95	19.90
116	F	H	H	H	Cl	254-257° C.	Calcd. for $C_{11}H_6Cl_2FN_5O_2S$:	36.48	1.67	19.34
							Found:	37.21	1.91	18.74
117	F	H	H	H	F	224-226° C.	Calcd. for $C_{11}H_6ClF_2N_5O_2S$:	38.21	1.75	20.26
							Found:	38.32	1.44	20.18
118	CF_3	H	H	H	H	179-180° C.	Calcd. for $C_{12}H_7ClF_3N_5O_2S$:	38.15	1.87	18.54
							Found:	38.19	1.59	18.00
119	Cl	H	H	H	CH_3	223-226° C.	Calcd. for $C_{12}H_9Cl_2N_5O_2S$:	40.23	2.53	19.55
							Found:	40.44	2.06	19.27
120	CF_3	H	H	H	OCH_3	205-206° C.	Calcd. for $C_{13}H_9ClF_3N_5O_3S$:	38.29	2.22	17.18
							Found:	38.03	2.35	17.39
121	Cl	H	H	H	H	188-189° C.	Calcd. for $C_{11}H_7Cl_2N_5O_2S$:	38.39	2.05	20.35
							Found:	38.26	1.84	19.98
122	COOMe	H	H	H	H	187-188° C.	Calcd. for $C_{13}H_{10}ClN_5O_4S$:	42.46	2.74	19.04
							Found:	42.54	2.79	19.13
123	SO_2NMe_2	H	H	H	H	164-165° C.	Calcd. for $C_{13}H_{13}ClN_6O_4S_2$:	37.46	3.14	20.16
							Found:	37.42	3.21	20.25

TABLE IV-continued



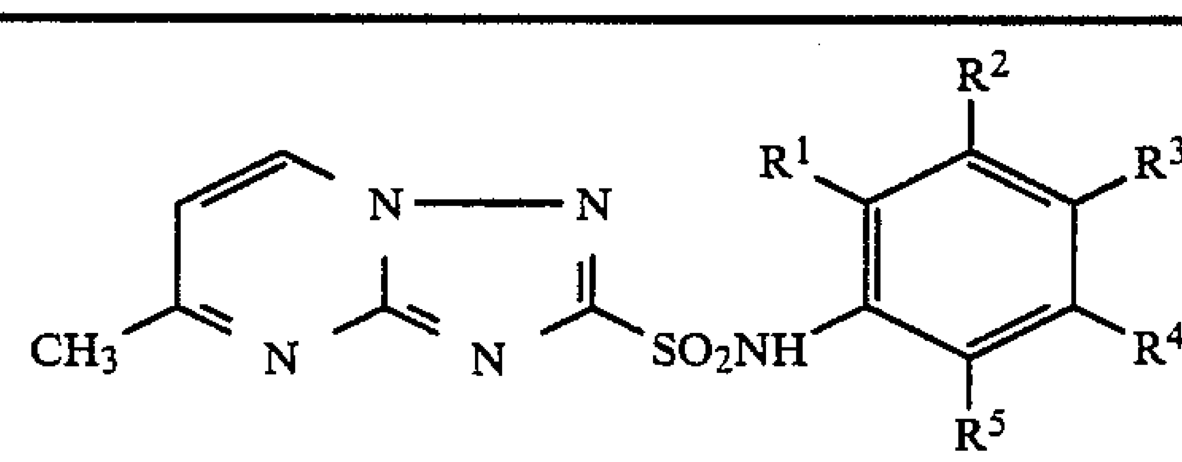
Cmpd.	R¹	R²	R³	R⁴	R⁵	Melting Point	Elemental Analysis: Analysis	C	H	N
124	H	Br	H	H	H	245–247° C.	Calcd. for $C_{11}H_7BrClN_5O_2S$:	34.00	1.82	18.02
							Found:	34.49	1.90	18.31
125	H	H	CF_3	H	H	239–241° C.	Calcd. for $C_{12}H_7F_3ClN_5O_2S$:	38.16	1.87	18.54
							Found:	38.54	1.83	18.83
126	$CONMe_2$	H	H	H	H	162–163° C.	Calcd. for $C_{14}H_{13}ClN_6O_3S$:	44.16	3.44	22.07
							Found:	44.57	3.47	22.43
127	COOiPr	H	H	H	H	158–160° C.	Calcd. for $C_{15}H_{14}ClN_5O_4S$:	45.52	3.57	17.69
							Found:	45.54	3.49	17.93
128	Cl	H	H	H	Ph	243–245° C.	Calcd. for $C_{17}H_{11}Cl_2N_5O_2S$:	48.58	2.64	16.66
							Found:	49.24	2.62	16.65
129	CH_3	H	H	H	H	170–171° C.	Calcd. for $C_{12}H_{10}ClN_5O_2S$:	44.52	3.11	21.63
							Found:	44.66	3.04	21.96
130	H	H	n-Bu	H	H	233–235° C.	Calcd. for $C_{15}H_{16}ClN_5O_2S$:	49.25	4.41	19.14
							Found:	49.10	4.30	19.30
131	H	OCH_3	H	H	H	212–215° C.	Calcd. for $C_{12}H_{10}ClN_5O_3S$:	42.42	2.97	20.61
							Found:	42.33	2.97	20.65
132	$SO_2N(Me)Et$	H	H	H	H	155–157° C.	Calcd. for $C_{14}H_{15}ClN_6O_4S_2$:	39.02	3.51	19.50
							Found:	39.17	3.47	19.54
133	F	H	H	H	H	171–172° C.	Calcd. for $C_{11}H_7ClFN_5O_2S$:	40.32	2.15	21.37
							Found:	41.00	2.18	21.55
134	H	SCH_3	H	H	H	210–212° C.	Calcd. for $C_{12}H_{10}ClN_5O_2S_2$:	40.51	2.83	19.68
							Found:	39.29	2.77	19.70

TABLE V



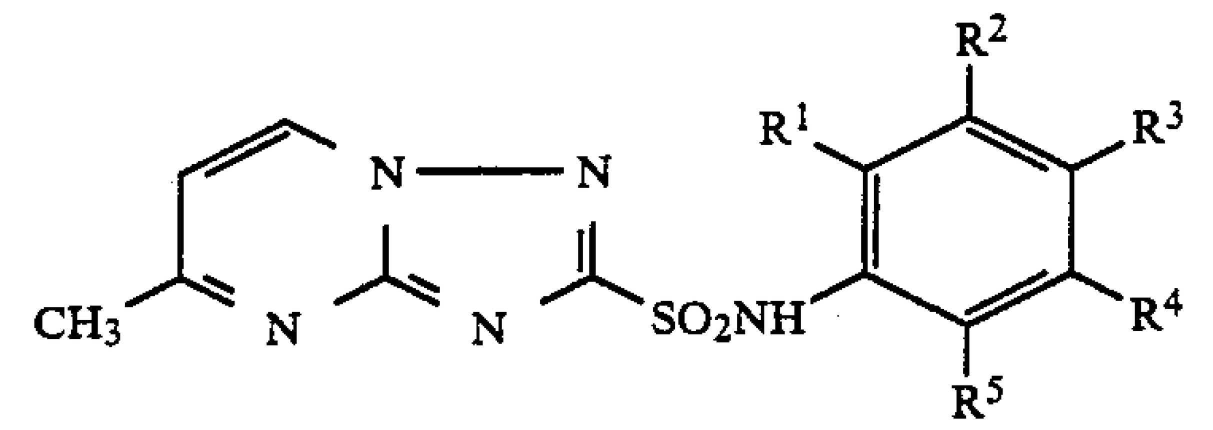
Cmpd.	R¹	R²	R³	R⁴	R⁵	Melting Point	Elemental Analysis: Analysis	C	H	N
135	$-SCH_3$	H	H	H	H	162.5–165° C.	Calcd. for $C_{12}H_{11}N_5O_2S_2$:	44.85	3.43	21.78
						(decomp.)	Found:	44.35	3.43	22.08
136	$-CF_3$	H	H	H	H	168.5–171° C.	Calcd. for $C_{12}H_8F_3N_5O_2S_2$:	42.11	2.33	20.45
						(decomp.)	Found:	41.93	2.28	19.99
137	Cl	H	H	H	Cl	278–280° C.	Calcd. for $C_{11}H_7Cl_2N_5O_2S$:	38.38	2.03	20.35
							Found:	38.28	1.70	20.75
138	F	H	H	H	F	296–299° C.	Calcd. for $C_{11}H_7F_2N_5O_2S$:	42.46	2.25	22.52
						(decomp.)	Found:	42.27	2.30	22.60
139	Cl	CH_3	H	H	Cl	252–255° C.	Calcd. for $C_{12}H_9Cl_2N_5O_2S$:	40.23	2.51	19.55
						(decomp.)	Found:	40.00	2.65	19.75
140	F	CH_3	H	H	F	280–283° C.	Calcd. for $C_{12}H_9F_2N_5O_2S$:	44.32	2.77	21.55
						(decomp.)	Found:	44.10	2.81	21.55
141	CF_3	H	H	H	OCH_3	230–232° C.	Calcd. for $C_{13}H_{10}F_3N_5O_3S$:	41.80	2.68	18.78
							Found:	41.80	2.77	18.69

TABLE VI



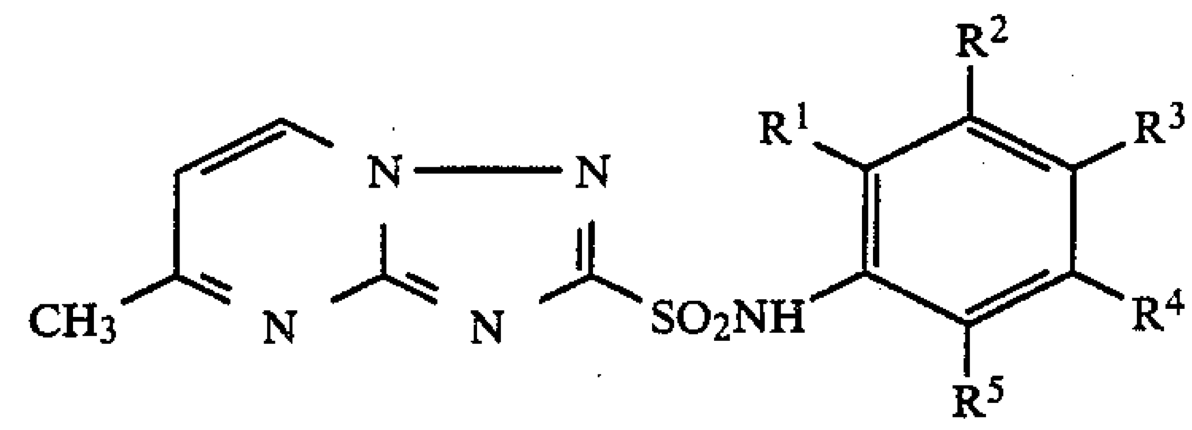
Cmpd.	R¹	R²	R³	R⁴	R⁵	Melting Point	Elemental Analysis: Analysis	C	H	N	S
142	$-SCH_3$	H	H	H	H	166°–169° C.	Calcd. for $C_{13}H_{13}N_5O_2S_2$:	45.67	3.77	20.11	
							Found:	47.34	3.90	19.86	

TABLE VI-continued



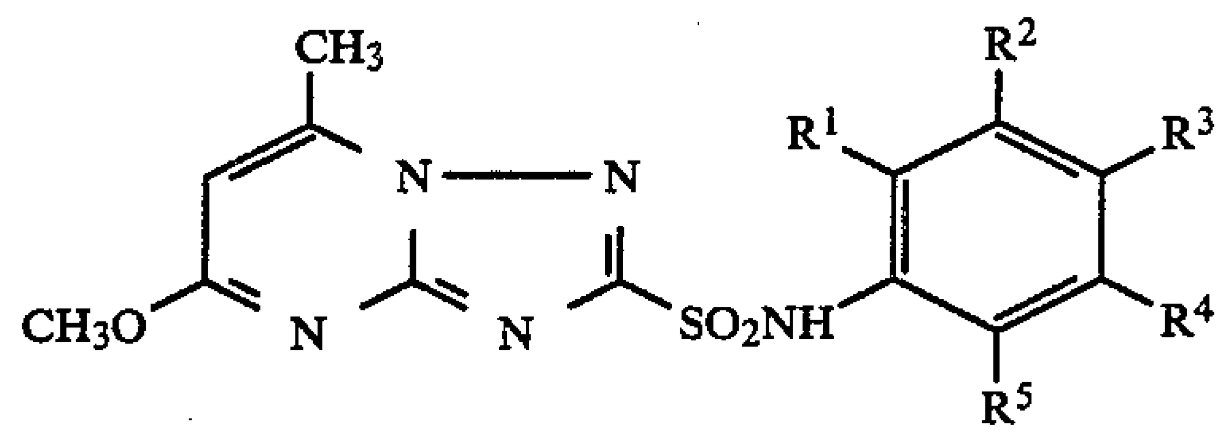
Cmpd.	R^1	R^2	R^3	R^4	R^5	Melting Point	Elemental Analysis				
143	—Cl	H	H	H	—Cl	228.5°-230° C.	Calcd. for $C_{12}H_9Cl_2N_5O_2S$:	40.24	2.51	19.54	
							Found:	40.34	2.52	19.09	
144	—Cl	H	H	H	—CH_3	211-215° C.	Calcd. for $C_{13}H_{12}ClN_5O_2S$:	46.19	3.55	20.72	
						(decomp.)	Found:	45.91	3.43	20.70	
145	CF_3	H	H	H	H	144–145° C.	Calcd. for $C_{13}H_{10}F_3N_5O_2S$:	43.67	2.79	19.59	
							Found:	43.67	2.74	19.52	
146	COOMe	H	H	H	CH_3	184–186° C.	Calcd. for $C_{15}H_{15}N_5O_4S$:	49.84	4.15	19.38	
							Found:	49.65	4.13	19.45	
147	Cl	CH_3	H	H	Cl	140° C.	Calcd. for $C_{12}H_{11}Cl_2N_5O_2S$:	41.91	2.95	18.80	
						(decomp.)	Found:	41.92	2.83	18.45	
148	Br	H	H	H	CH_3	106° C.	Calcd. for $C_{13}H_{12}BrN_5O_2S$:	40.83	3.14	18.32	
						(decomp.)	Found:	40.36	3.14	18.30	
149	$SOCF_2CF_2H$	H	H	H	H	180° C.	Calcd. for $C_{14}H_{11}F_4N_5O_3S_2$:	38.40	2.52	16.03	
						(decomp.)	Found:	36.70	2.50	14.69	
150	SCH_3	H	H	H	CH_3	234° C.	Calcd. for $C_{14}H_{15}N_5O_2S_2$:	48.12	4.33	20.04	
						(decomp.)	Found:	47.89	4.17	20.31	
151	NO_2	H	H	H	CH_3	120° C.	Calcd. for $C_{13}H_{12}N_6O_4S$:	44.82	3.47	24.13	
						(decomp.)	Found:	45.94	3.30	23.75	
152	Br	H	H	H	Cl	230–235° C.	Calcd. for $C_{12}H_9BrClN_5O_2S$:	35.79	2.25	17.39	
							Found:	35.50	2.19	17.97	
153	I	H	H	H	Cl	210–215° C.	Calcd. for $C_{12}H_9ClIN_5O_2S$:	32.05	2.02	15.58	
							Found:	32.36	2.29	15.31	
154	Cl	H	H	H	Ph	233–243° C.	Calcd. for $C_{18}H_{14}ClN_5O_2S$:	54.07	3.53	17.52	8.02
						(decomp.)	Found:	53.49	3.45	17.82	8.49
155	Cl	Cl	H	H	CH_3	256–259° C.	Calcd. for $C_{13}H_{11}Cl_2N_5O_2S$:	41.95	2.98	18.81	8.61
						(decomp.)	Found:	42.00	2.96	18.75	8.63
156	$COOCH_3$	H	H	Cl	CH_3	75–80° C.	Calcd. for $C_{15}H_{14}ClN_5O_4S$:	45.52	3.57	17.69	8.10
							Found:	45.28	3.57	17.41	8.07
157	F	H	H	H	F	245–247° C.	Calcd. for $C_{12}H_9F_2N_5O_2S$:	44.30	2.79	21.53	
							Found:	44.69	2.80	21.85	
158	F	H	H	H	Cl	243–248° C.	Calcd. for $C_{12}H_9ClFN_5O_2S$:	42.17	2.65	20.49	
							Found:	42.14	2.63	20.18	
159	COOMe	H	H	H	F	159–163° C.	Calcd. for $C_{14}H_{12}FN_5O_4S$:	46.03	3.31	19.16	
							Found:	45.56	3.08	19.25	
160	NO_2	H	H	CH_3	CH_3	225–230° C.	Exact mass calcd. for $C_{14}H_{14}N_6O_4S$:			262.0799	
							Found:			262.0802	
							Analysis	C	H	N	S
161	F	H	H	H	SCH_3	190–192° C.	Calcd. for $C_{13}H_{12}FN_5O_2S_2$:	44.18	3.42	19.82	
							Found:	44.02	3.41	19.51	
162	F	H	H	H	CH_3	241° C.	Calcd. for $C_{13}H_{12}FN_5O_2S$:	48.59	3.76	21.80	
						(decomp.)	Found:	48.31	3.51	21.62	
163	F	F	H	F	F	209° C.	Calcd. for $C_{12}H_7F_4N_5O_2S$:	39.89	1.95	19.39	
						(decomp.)	Found:	38.41	2.21	19.04	
164	CH_2OCH_3	H	H	H	Cl	186–191° C.	Calcd. for $C_{14}H_{14}ClN_5O_3S$:	45.72	3.84	19.03	
						(decomp.)	Found:	45.46	3.88	18.97	
165	CN	H	H	H	CH_3	240–245° C.	Calcd. for $C_{14}H_{12}N_6O_2S$:	51.22	3.68	25.59	9.77
						(decomp.)	Found:	49.43	3.58	24.55	9.47
166	$COCH_3$	H	H	H	CH_3	204–207° C.	Calcd. for $C_{15}H_{15}N_5O_3S$:	52.17	4.38	20.27	9.28
							Found:	51.82	4.25	20.95	9.19
167	CN	H	H	H	F	201–203° C.	Calcd. for $C_{13}H_9FN_6O_2S$:	46.98	2.73	25.29	
							Found:	46.41	2.81	26.01	
168	CF_3	H	H	H	F	214–216° C.	Calcd. for $C_{13}H_9F_4N_5O_2S$:	41.60	2.42	18.66	
							Found:	41.33	2.61	18.74	
169	CF_3	H	Cl	H	H	170–171° C.	Calcd. for $C_{13}H_9ClF_3N_5O_2S$:	39.85	2.32	17.88	
							Found:	39.96	2.29	17.30	
170	Cl	OCH_3	H	H	Cl	229–231° C.	Calcd. for $C_{13}H_{11}Cl_2N_5O_3S$:	40.21	2.86	18.04	
						(decomp.)	Found:	40.18	2.99	17.71	
171	F	H	H	H	OCH_3	212–214° C.	Calcd. for $C_{13}H_{12}FN_5O_3S$:	46.28	3.58	20.76	
							Found:	46.26	3.56	20.49	
172	F	OCH_3	H	H	F	219–221° C.	Calcd. for $C_{13}H_{11}F_2N_5O_3S$:	43.94	3.12	19.71	
							Found:	43.79	3.29	19.48	
173	F	H	H	H	NO_2	227° C.	Calcd. for $C_{12}H_9FN_6O_2S$:	44.99	2.83	26.24	
						(decomp.)	Found:	44.63	2.51	26.46	
174	F	CH_3	H	H	F	219–221° C.	Calcd. for $C_{13}H_{11}F_2N_5O_2S$:	46.01	3.27	20.64	
							Found:	46.27	3.47	20.27	
175	CF_3	H	H	H	OCH_3	209–211° C.	Calcd. for $C_{14}H_{12}F_3N_5O_3S$:	43.41	3.12	18.08	
							Found:	43.31	3.07	17.97	
176	CF_3	H	H	H	CH_2SCH_3	227–229° C.	Calcd. for $C_{15}H_{14}F_3N_5O_2S_2$:	43.16	3.38	16.78	
							Found:	43.24	3.71	16.37	
177	CF_3	H	H	H	CH_3	219–220° C.	Calcd. for $C_{14}H_{12}F_3N_5O_2S$:	48.41	3.48	20.17	

TABLE VI-continued



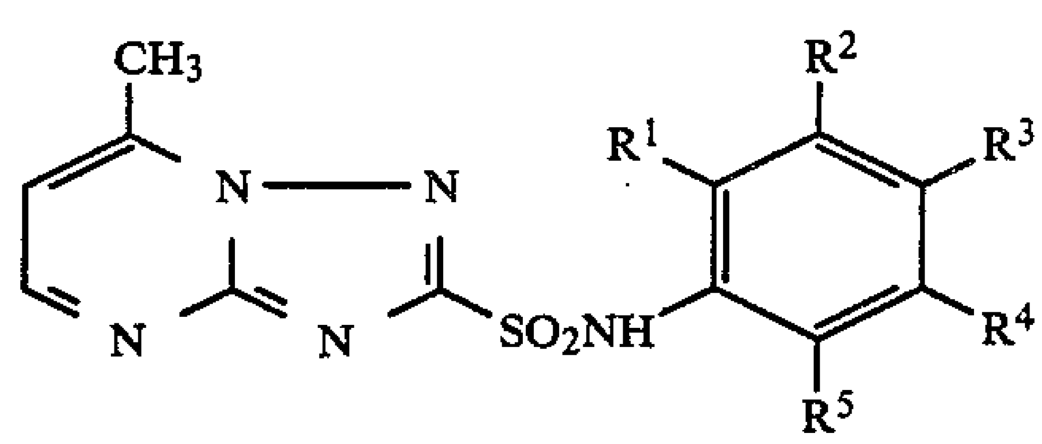
Cmpd.	R¹	R²	R³	R⁴	R⁵	Melting Point	Elemental Analysis			
							Found:	48.14	3.71	20.34

TABLE VII



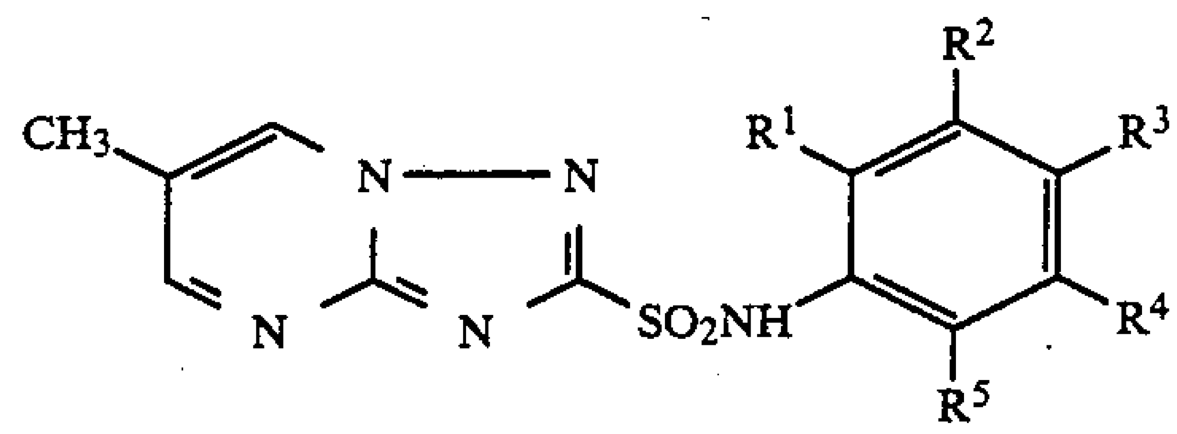
Cmpd.	R^1	R^2	R^3	R^4	R^5	Melting Point	Elemental Analysis: Analysis	C	H	N
178	Cl	H	H	H	Cl	133°-134.5° C.	Calcd. for $C_{13}H_{11}Cl_2N_5O_3S$:	40.22	2.83	18.03
179	Cl	H	H	H	H	195-196° C.	Found:	40.05	2.88	17.86

TABLE VIII



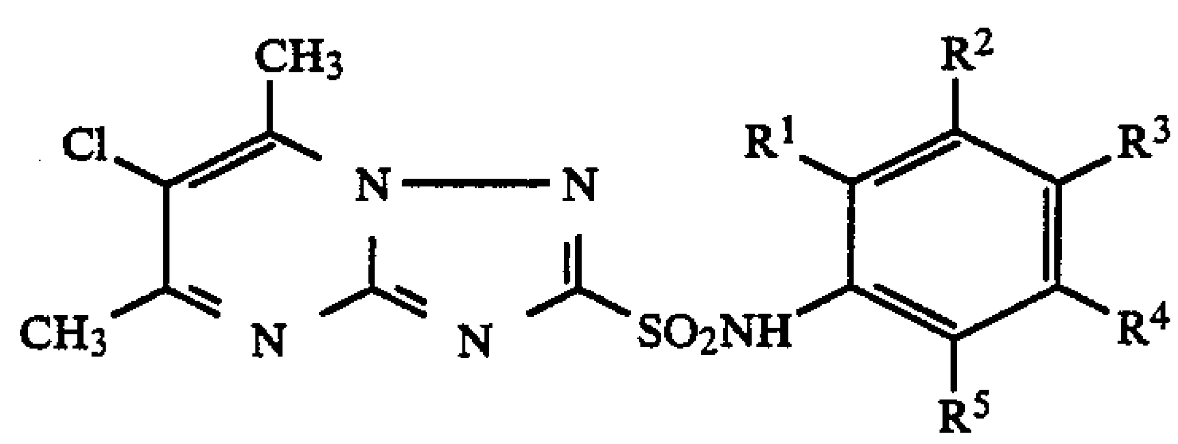
Cmpd.	R^1	R^2	R^3	R^4	R^5	Melting Point	Elemental Analysis: Analysis	C	H	N
180	Cl	H	H	H	Cl	268°-269.5° C.	Calcd. for $C_{12}H_9Cl_2N_5O_2S$:	40.24	2.51	19.54
						(decomp.)	Found:	40.19	2.68	19.06
181	F	H	H	H	Cl	270-273° C.	Calcd. for $C_{12}H_9ClFN_5O_2S$:	42.17	2.65	20.49
							Found:	42.09	2.63	19.91
182	Cl	CH_3	H	H	Cl	257-263° C.	Calcd. for $C_{13}H_{11}Cl_2N_5O_2S$:	41.91	2.98	18.82
							Found:	41.88	2.86	18.30
183	CF_3	H	H	H	H	171-185° C.	Calcd. for $C_{13}H_{10}F_3N_5O_2S$:	43.70	2.82	19.60
							Found:	42.33	2.66	19.36
184	NO_2	H	H	H	CH_3	200-205° C.	Calcd. for $C_{13}H_{12}N_6O_4S$:	44.82	3.47	24.13
							Found:	44.43	3/43	23.81
185	F	H	H	H	F	255-257° C.	Calcd. for $C_{12}H_9F_2N_5O_2S$:	44.30	2.79	21.53
							Found:	44.08	3.08	21.32
186	Cl	H	H	H	CH_3	229.5-233° C.	Calcd. for $C_{13}H_{12}ClN_5O_2S$:	46.22	3.58	20.74
							Found:	45.56	3.93	20.27
187	$COOCH_3$	H	H	H	F	200-201° C.	Calcd. for $C_{14}H_{12}FN_5O_4S$:	46.03	3.31	19.17
							Found:	45.75	3.25	19.20
188	NO_2	H	H	CH_3	CH_3	233-236° C.	Calcd. for $C_1H_{14}N_6O_4S$:	46.40	3.89	23.19
							Found:	46.29	3.67	22.84
189	$COOCH_3$	H	H	H	CH_3	167-167.5° C.	Calcd. for $C_{15}H_{15}N_5O_4S$:	49.86	4.18	19.38
							Found:	49.78	4.10	19.16
190	F	CH_3	H	H	F	256-258° C.	Calcd. for $C_{13}H_{11}F_2N_5O_2S$:	46.02	3.27	20.64
							Found:	44.95	3.00	20.00
191	CF_3	H	H	H	OCH_3	260-262° C.	Calcd. for $C_{14}H_{12}F_3N_5O_3S$:	43.41	3.12	18.08
							Found:	42.83	3.18	19.74

TABLE IX



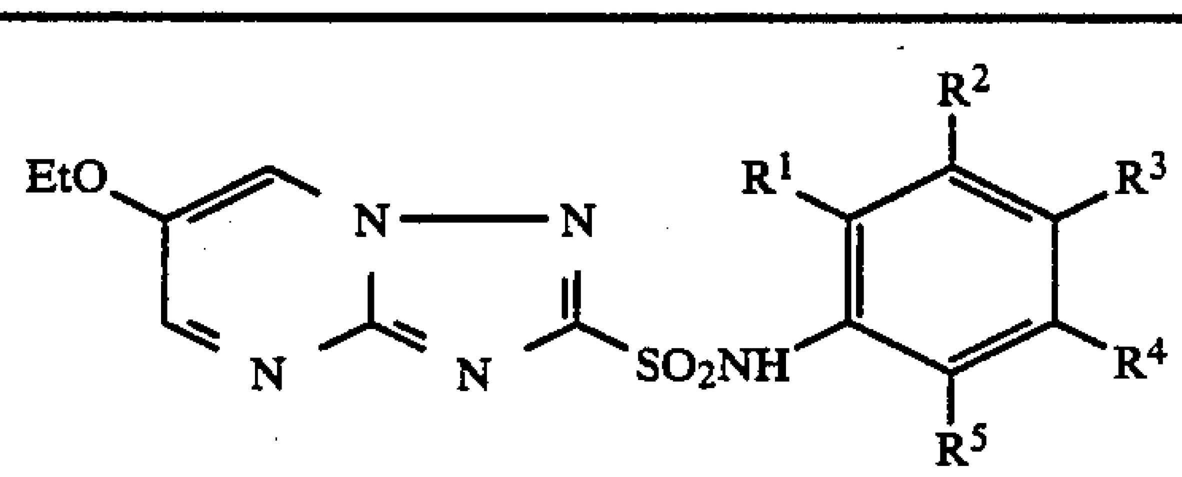
Cmpd.	R^1	R^2	R^3	R^4	R^5	Melting Point	Analysis	C	H	N	S
							Elemental Analysis				
192	Cl	H	H	H	Cl	249° C. (decomp.)	Calcd. for $C_{12}H_{10}Cl_2N_5O_2S$:	40.21	40.21	19.56	8.94
							Found:	39.99	2.66	19.62	8.70
193	F	H	H	H	F	263–265° C.	Calcd. for $C_{12}H_9F_2N_5O_2S$:	44.30	2.79	21.53	9.86
							Found:	44.37	2.92	20.98	9.85
194	Cl	CH_3	H	H	Cl	276–280° C.	Calcd. for $C_{13}H_{11}Cl_2N_5O_2S$:	41.94	2.98	18.82	8.61
							Found:	41.59	2.97	19.13	8.46
195	Cl	H	H	H	CH_3	227–232° C.	Calcd. for $C_{13}H_{12}ClN_5O_2S$:	46.22	3.58	20.74	9.49
							Found:	45.73	3.47	20.94	9.49
196	NO_2	H	H	H	CH_3	251–253° C.	Calcd. for $C_{13}H_{12}N_6O_4S$:	44.82	3.47	24.13	9.20
							Found:	43.84	3.39	24.05	9.28
197	COOMe	H	H	H	CH_3	208.5–210.5° C.	Calcd. for $C_{15}H_{15}N_5O_4S$:	49.85	4.18	19.38	
							Found:	49.96	4.14	19.75	

TABLE X



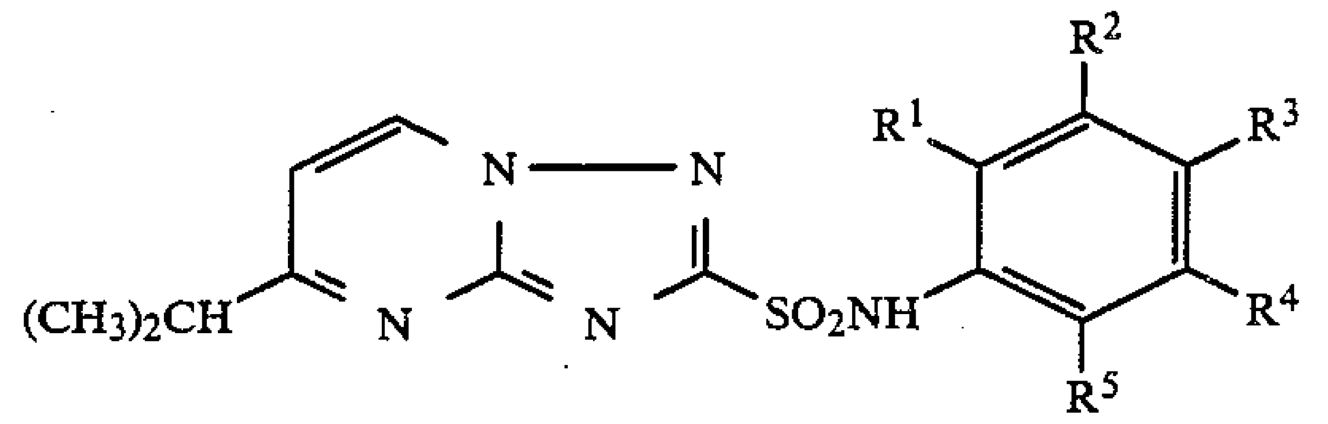
Cmpd.	R^1	R^2	R^3	R^4	R^5	Melting Point	Analysis	C	H	N
							Elemental Analysis			
198	Cl	H	H	H	H	174–176° C.	Calcd. for $C_{13}H_{11}Cl_2N_5O_2S$:	41.95	2.98	18.82
							Found:	41.64	2.84	18.54
199	Cl	CH_3	H	H	Cl	231–233° C.	Calcd. for $C_{14}H_{12}Cl_3N_5O_2S$:	39.96	2.88	18.65
							Found:	39.94	2.88	18.15
200	Cl	H	H	H	Cl	171° C. (decomp.)	Calcd. for $C_{13}H_{10}Cl_3N_5O_2S$:	38.39	2.48	17.22
							Found:	38.47	2.66	17.37

TABLE XI



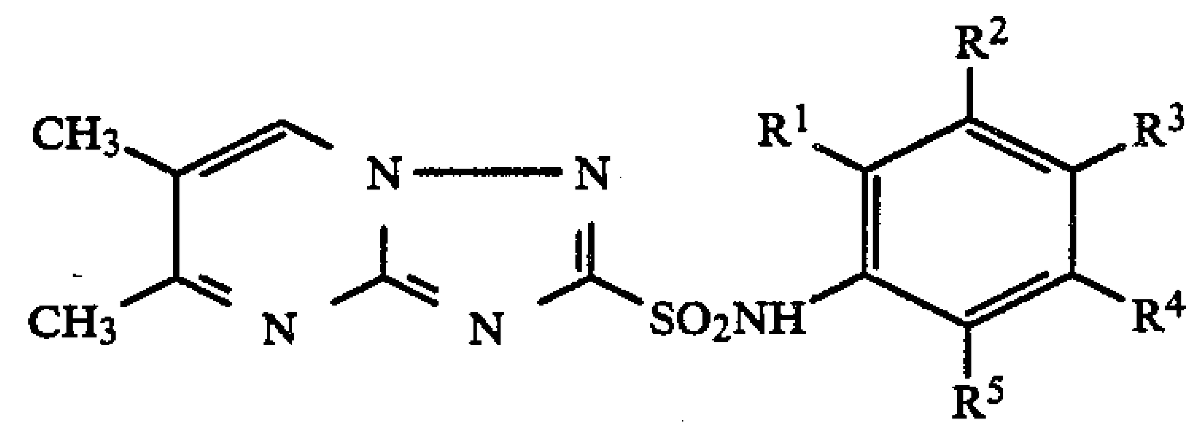
Cmpd.	R^1	R^2	R^3	R^4	R^5	Melting Point	Analysis	C	H	N
							Elemental Analysis			
201	CF_3	H	H	H	H	75–78° C. (decomp.)	Calcd. for $C_{14}H_{12}F_3N_5O_3S$:	43.36	3.09	18.06
							Found:	43.53	3.17	17.50
202	Cl	H	H	H	CH_3	105–110° C. (decomp.)	Calcd. for $C_{14}H_{14}ClN_5O_3S$:	45.66	3.80	19.02
							Found:	43.74	3.80	18.76
203	Cl	H	H	H	Cl	215–216° C.	Calcd. for $C_{12}H_{12}Cl_2N_5O_2S$:	40.21	2.83	18.04
							Found:	40.13	2.96	17.99

TABLE XII



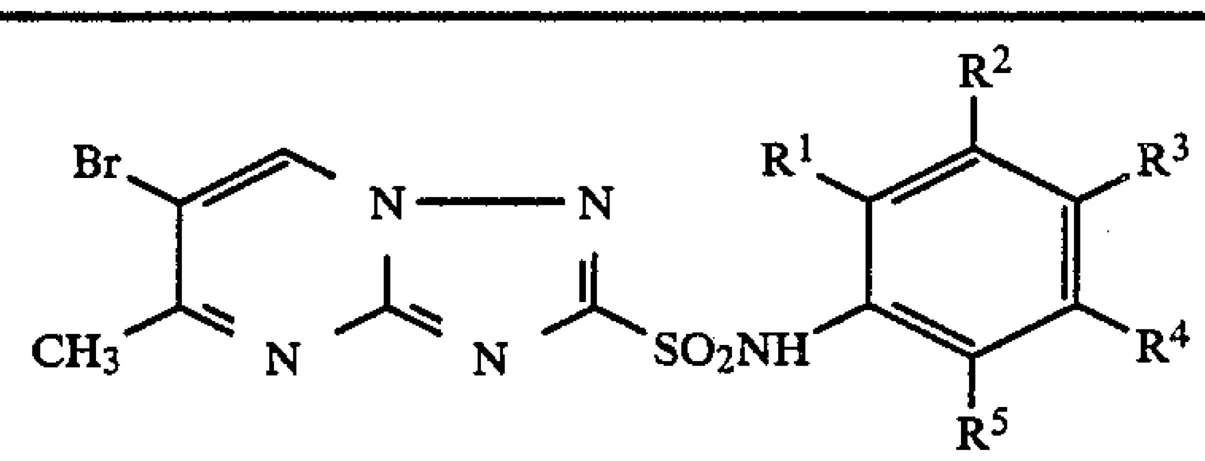
Cmpd.	R¹	R²	R³	R⁴	R⁵	Melting Point	Elemental Analysis: Analysis	C	H	N	S
204	Cl	H	H	H	Cl	214–216° C.	Calcd. for $C_{14}H_{13}Cl_2N_5O_2S$:	43.51	3.37	18.13	8.30
							Found:	43.50	3.28	17.63	7.96

TABLE XIII



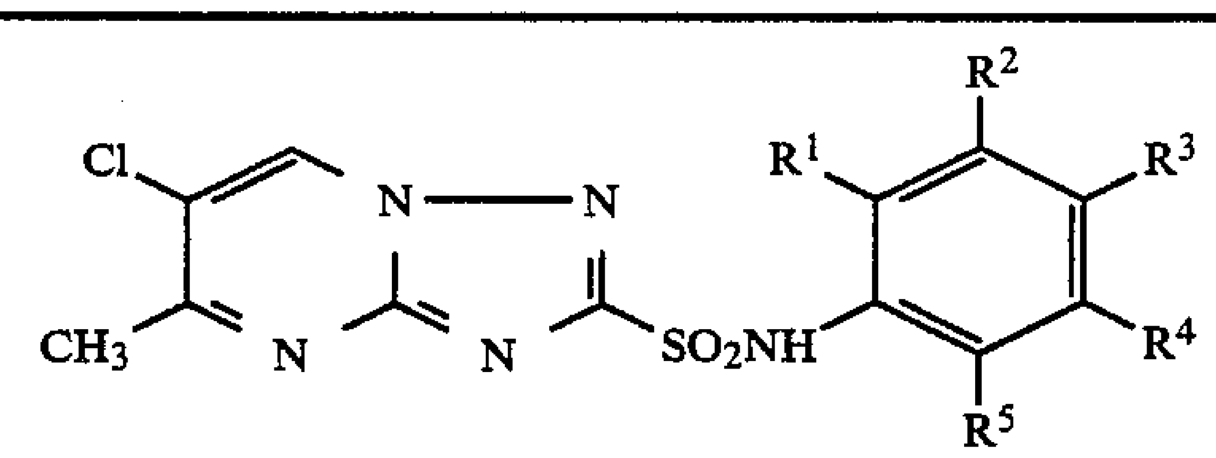
Cmpd.	R¹	R²	R³	R⁴	R⁵	Melting Point	Elemental Analysis: Analysis	C	H	N
205	Cl	H	H	H	Cl	235-237° C.	Calcd. for $C_{13}H_{11}Cl_2N_5O_2S$:	41.93	2.95	18.81
							Found:	41.80	3.08	18.65

TABLE XIV



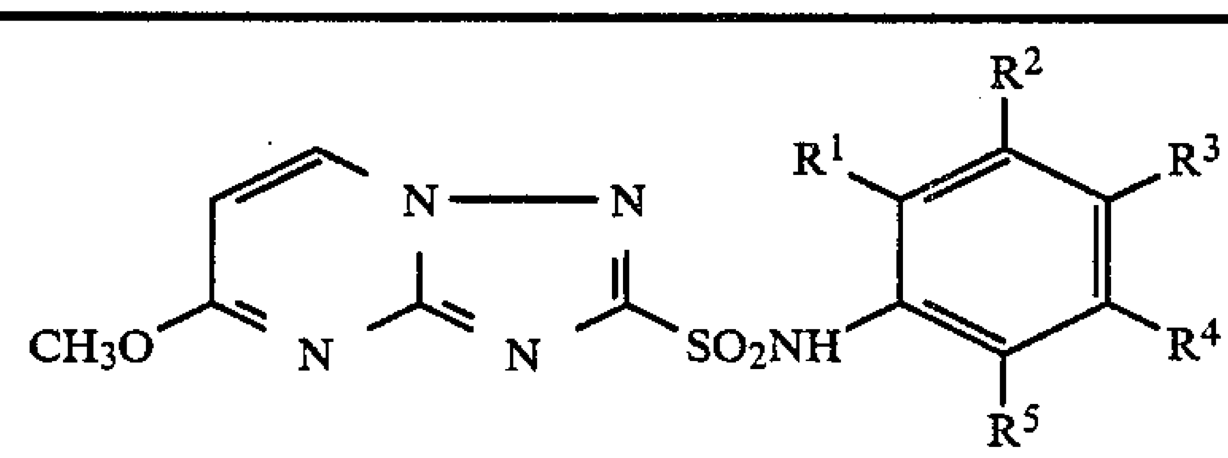
Cmpd.	R¹	R²	R³	R⁴	R⁵	Melting Point	Elemental Analysis	
206	Cl	H	H	H	Cl	215-216° C.	Exact mass calcd. for $C_{12}H_8BrCl_2N_5O_2S$:	438.8898
							Found:	438.8899

TABLE XV



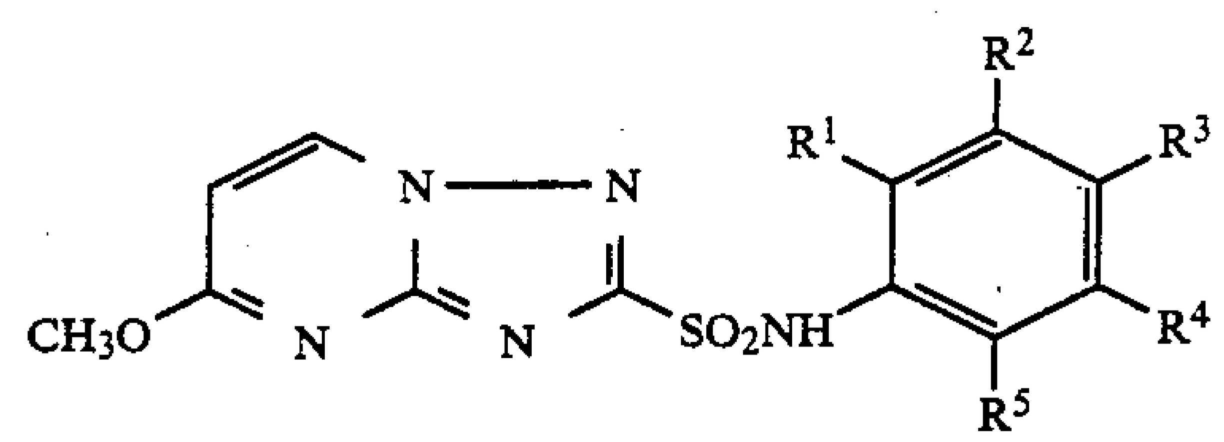
Cmpd.	R¹	R²	R³	R⁴	R⁵	Melting Point	Elemental Analysis: Analysis	C	H	N
207	Cl	H	H	H	Cl	105–110° C.	Calcd. for $C_{12}H_8Cl_3N_5O_2S$:	36.69	2.04	17.80
							Found:	36.28	2.15	18.41

TABLE XVI



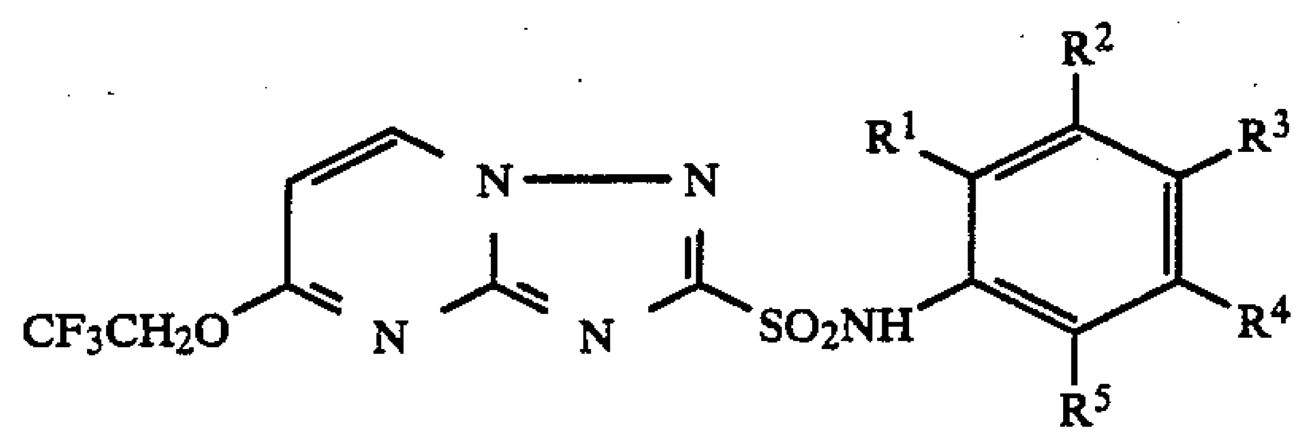
Cmpd.	R¹	R²	R³	R⁴	R⁵	Melting Point	Elemental Analysis: Analysis	C	N	H
208	Cl	H	H	H	Cl	235-237° C.	Calcd. for $C_{12}H_9Cl_2N_5O_3S$:	38.51	2.41	18.72

TABLE XVI-continued



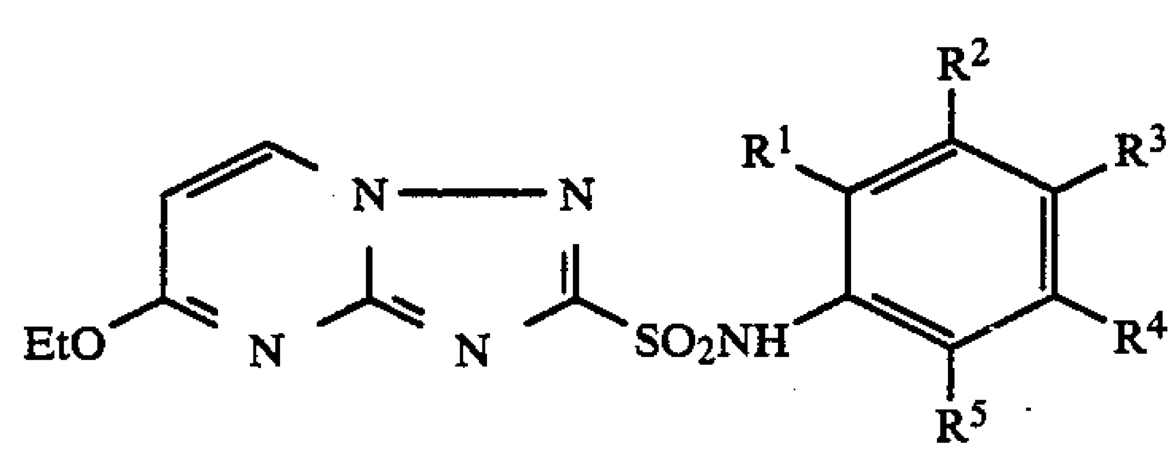
Cmpd.	R^1	R^2	R^3	R^4	R^5	Melting Point	Elemental Analysis: Analysis	C	N	H
							Found:	38.29	2.44	18.92

TABLE XVII



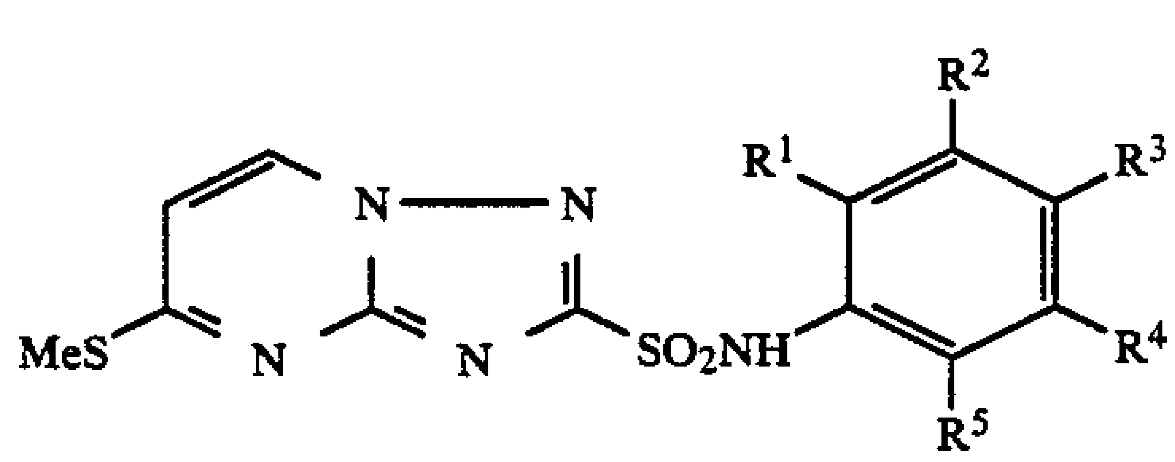
Cmpd.	R^1	R^2	R^3	R^4	R^5	Melting Point	Elemental Analysis: Analysis	C	H	N
209	Cl	H	H	H	Cl	266–269° C.	Calcd. for $C_{13}H_8Cl_2F_3N_5O_3S$:	35.29	1.81	15.84
							Found:	35.14	1.72	15.65

TABLE XVIII



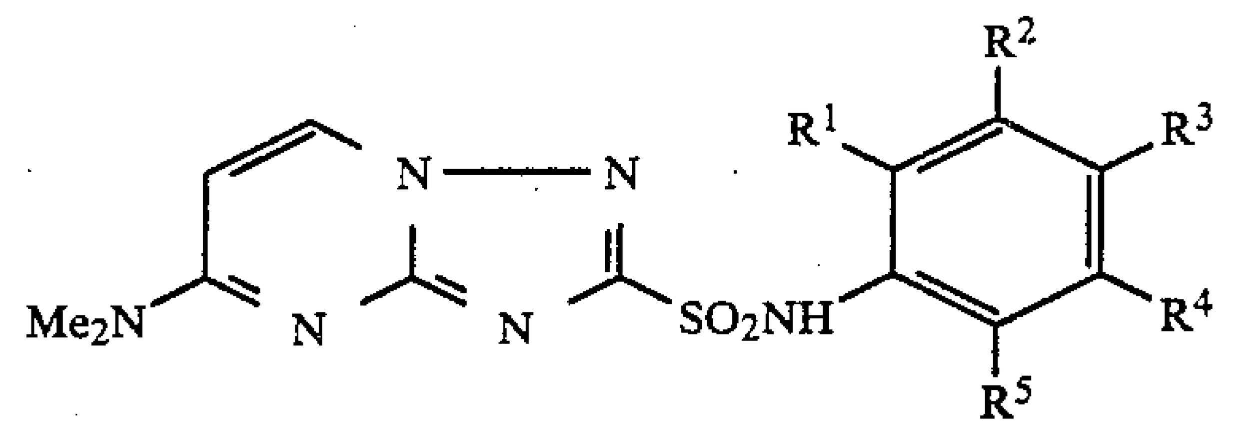
Cmpd.	R^1	R^2	R^3	R^4	R^5	Melting Point	Elemental Analysis: Analysis	C	H	N
210	Cl	H	H	H	Cl	230–233° C.	Calcd. for $C_{13}H_{11}Cl_2N_5O_3S$:	40.21	2.83	18.03
							Found:	40.10	2.76	17.87

TABLE XIX



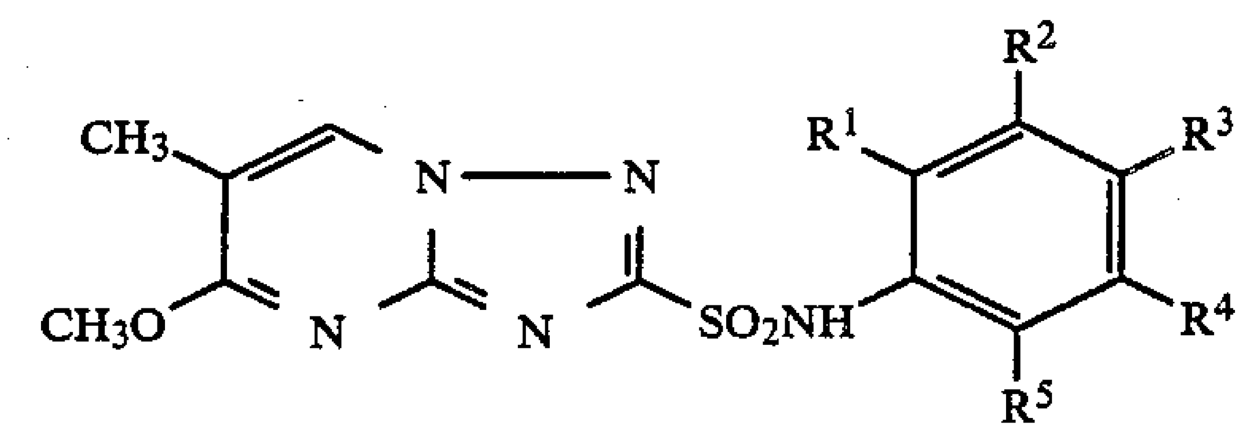
Cmpd.	R^1	R^2	R^3	R^4	R^5	Melting Point	Elemental Analysis: Analysis	C	H	N
211	Cl	H	H	H	Cl	239–243° C.	Calcd. for $C_{12}H_9Cl_2N_5O_2S_2$:	36.92	2.31	17.95
						(decomp.)	Found:	36.51	2.41	17.68

TABLE XX



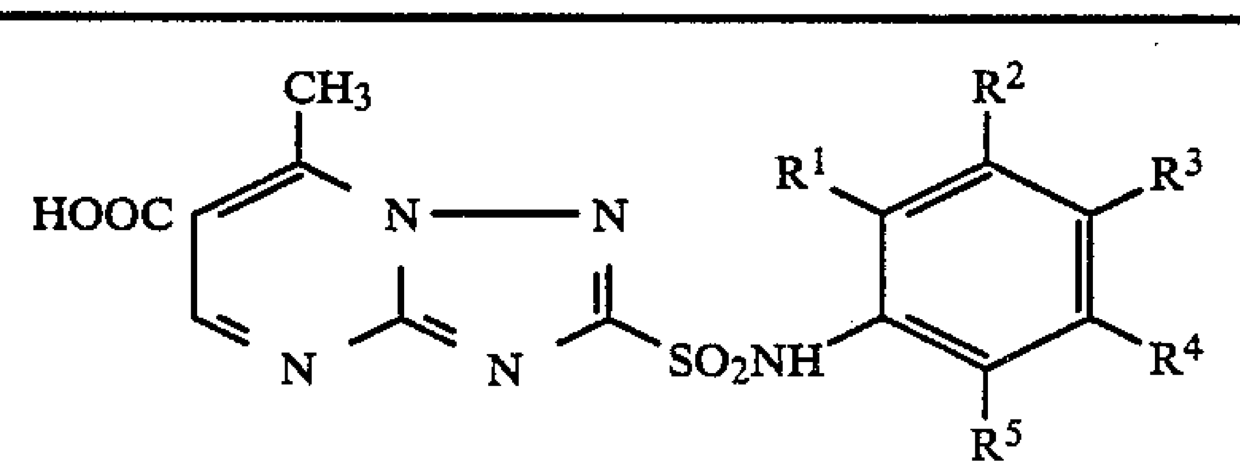
Cmpd.	R^1	R^2	R^3	R^4	R^5	Melting Point	Elemental Analysis Analysis	C	N	H	S
212	Cl	H	H	H	Cl	>310° C.	Calcd. for $C_{13}H_{12}Cl_2N_6O_2S$:	40.31	3.10	21.71	8.28
							Found:	40.31	3.05	22.31	7.99

TABLE XXI



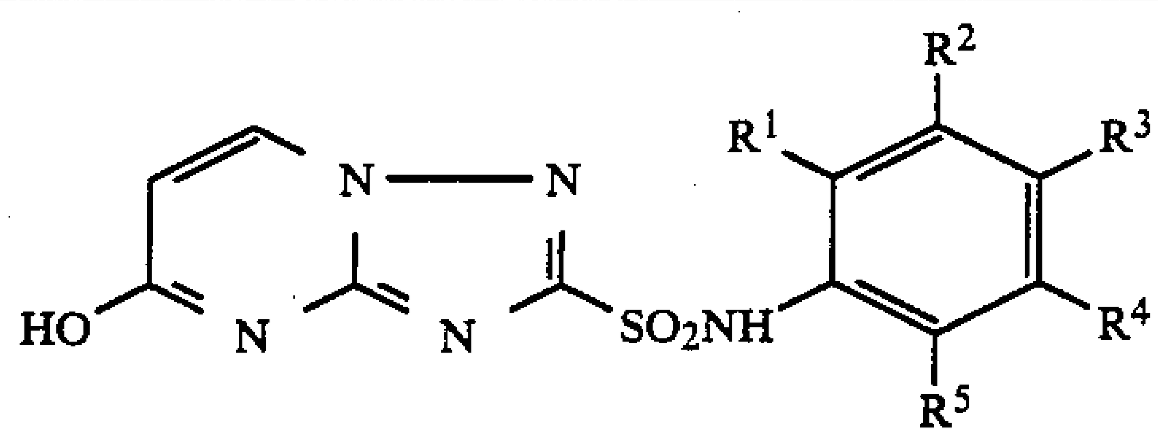
Cmpd.	R^1	R^2	R^3	R^4	R^5	Melting Point	Elemental Analysis Analysis	C	H	N
213	Cl	H	H	H	Cl	235–242° C.	Calcd. for $C_{13}H_{11}Cl_2N_5O_3S$:	40.21	2.84	18.04
						(decomp.)	Found:	40.37	2.78	18.06
214	F	H	H	H	F	230–232° C.	Calcd. for $C_{13}H_{11}F_2N_5O_3S$:	43.94	3.12	19.71
							Found:	43.80	3.10	20.11
215	$COOCH_3$	H	H	H	F	195–197° C.	Calcd. for $C_{15}H_{14}FN_5O_5S$:	45.57	3.57	17.71
							Found:	45.26	3.51	18.12
216	$COOCH_3$	H	H	H	CH_3	197–198° C.	Calcd. for $C_{16}H_{17}N_5O_5S$:	49.10	4.38	17.89
							Found:	48.95	4.28	17.88
217	CF_3	H	H	H	H	213–215° C.	Calcd. for $C_{14}H_{12}F_3N_5O_3S$:	43.41	3.12	18.08
							Found:	42.90	3.21	18.48
218	Cl	CH_3	H	H	Cl	240.5–241.5° C.	Calcd. for $C_{14}H_{13}Cl_2N_5O_3S$:	41.80	3.26	17.41
							Found:	41.64	3.28	17.56
219	F	CH_3	H	H	F	230–231° C.	Calcd. for $C_{14}H_{13}F_2N_5O_3S$:	45.53	3.55	18.96
							Found:	45.16	3.55	19.37
220	Cl	H	H	H	CH_3	213–214° C.	Calcd. for $C_{14}H_{14}ClN_5O_3S$:	45.72	3.84	19.04
							Found:	45.96	3.90	19.40
221	NO_2	H	H	H	CH_3	226–228° C.	Calcd. for $C_{14}H_{14}N_6O_5S$:	44.44	3.73	22.21
							Found:	44.52	3.75	22.50
222	NO_2	H	H	CH_3	CH_3	230–231° C.	Calcd. for $C_{15}H_{16}N_6O_5S$:	45.91	4.11	21.42
							Found:	45.49	4.04	21.64
223	CF_3	H	H	H	OCH_3	232–233° C.	Calcd. for $C_{15}H_{14}F_3N_5O_4S$:	43.17	3.38	16.78
							Found:	43.10	3.42	16.92

TABLE XXII



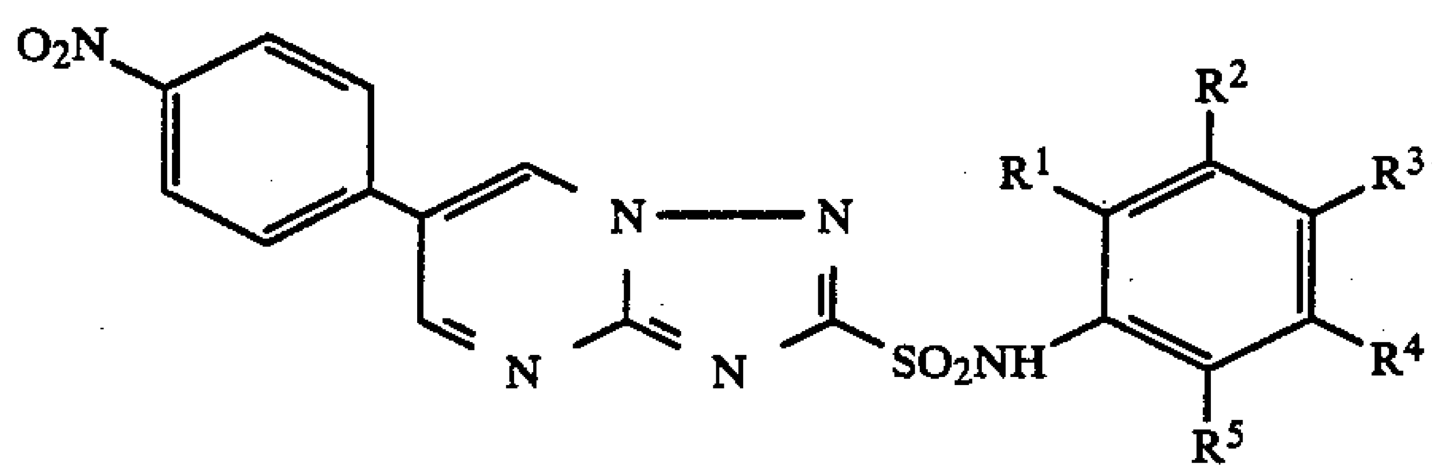
Cmpd.	R^1	R^2	R^3	R^4	R^5	Melting Point	Elemental Analysis Analysis	C	H	N
224	Cl	H	H	H	Cl	220° C.	Calcd. for $C_{13}H_9Cl_2N_5O_4S$:	38.80	2.24	17.41
						(decomp.)	Found:	39.30	2.66	17.41

TABLE XXIII



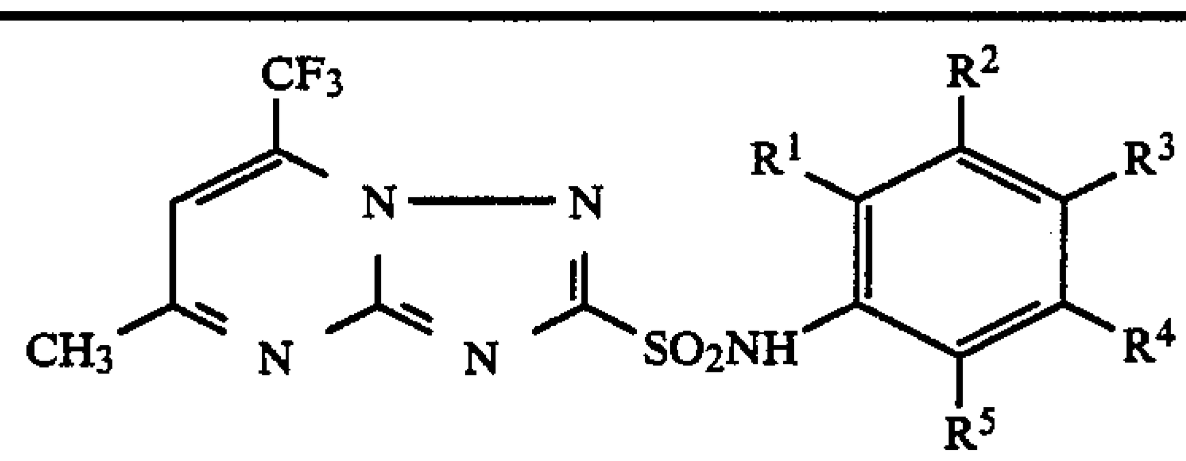
Cmpd.	R1	R2	R3	R4	R5	Melting Point	Elemental Analysis: Analysis	C	H	N
225	Cl	H	H	H	Cl	310–320° C. (decomp.)	Calcd. for $C_{11}H_7Cl_2N_5O_3S$:	36.65	1.94	19.40
							Found:	36.79	1.76	19.14

TABLE XXIV



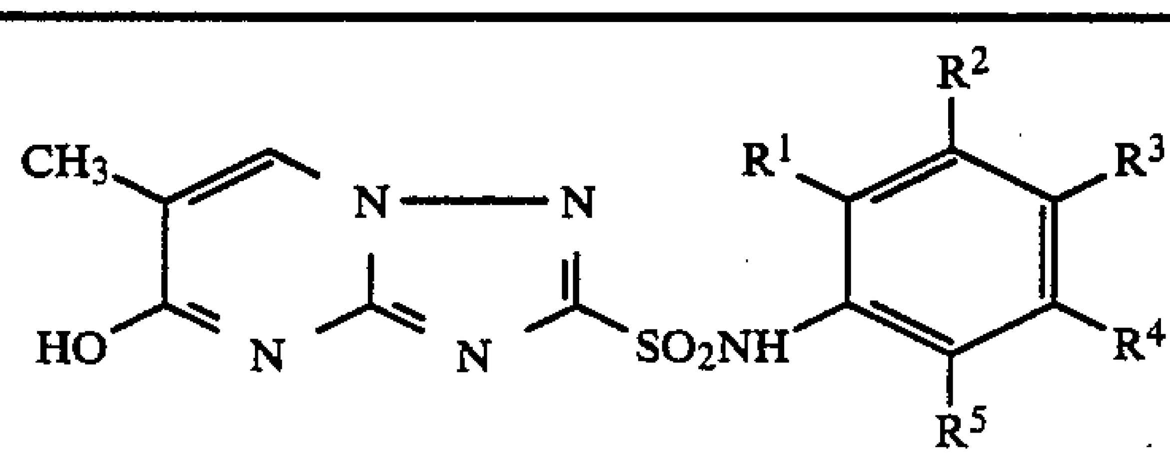
Cmpd.	R1	R2	R3	R4	R5	Melting Point	Elemental Analysis: Analysis	C	H	N
226	Cl	H	H	H	Cl	285–287° C.	Calcd. for $C_{17}H_{10}Cl_2N_6O_4S$:	43.84	2.15	18.00
							Found:	44.12	2.43	17.45

TABLE XXV



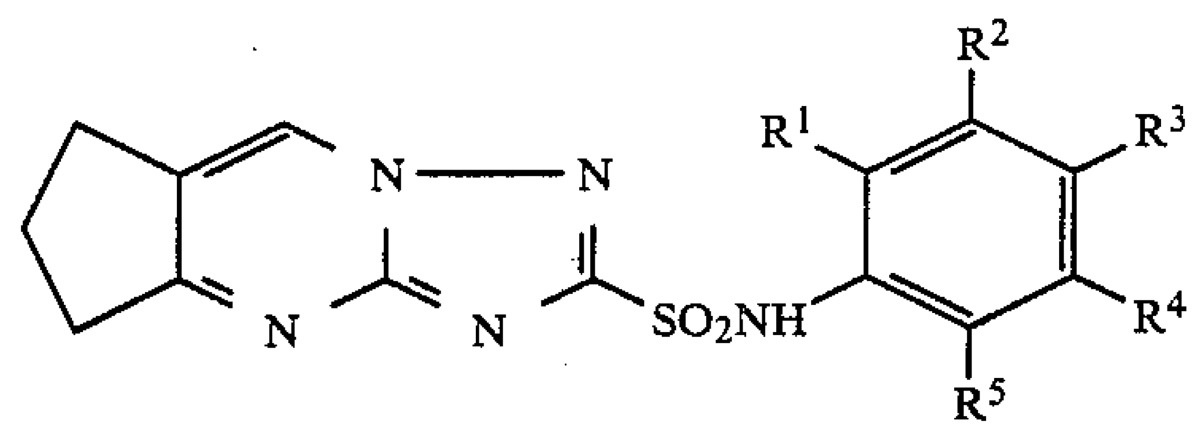
Cmpd.	R1	R2	R3	R4	R5	Melting Point	Elemental Analysis: Analysis	C	H	N
227	Cl	H	H	H	Cl	237–239° C.	Calcd. for $C_{13}H_8Cl_2F_3N_5O_2S$:	36.63	1.88	16.42
							Found:	36.74	1.52	16.94
228	F	H	H	H	F	234–237° C.	Calcd. for $C_{13}H_8F_5N_5O_2S$:	39.74	2.04	17.83
							Found:	39.49	2.08	18.11
229	Cl	CH_3	H	H	Cl	252–254° C.	Calcd. for $C_{14}H_{10}Cl_2F_3N_5O_2S$:	38.21	2.27	15.97
							Found:	38.09	2.34	16.40
230	F	CH_3	H	H	F	243–245° C.	Calcd. for $C_{14}H_{10}F_5N_5O_2S$:	41.32	2.46	17.23
							Found:	41.21	2.51	17.49
231	CF_3	H	H	H	OCH_3	226–229° C.	Calcd. for $C_{15}H_{11}F_6N_5O_3S$:	39.61	2.42	15.40
							Found:	39.50	2.52	15.60
307	Cl	H	H	H	CH_3	234–235° C.	Calcd. for $C_{14}H_{11}ClF_3N_5OS$:	41.14	2.73	17.26
							Found:	41.03	2.77	17.14
308	Cl	H	H	H	CH_2OCH_3	206–207° C.	Calc. for $C_{15}H_{13}ClF_3N_5O_3S$	41.34	3.01	16.07
							Found:	41.19	2.97	16.02

TABLE XXVI



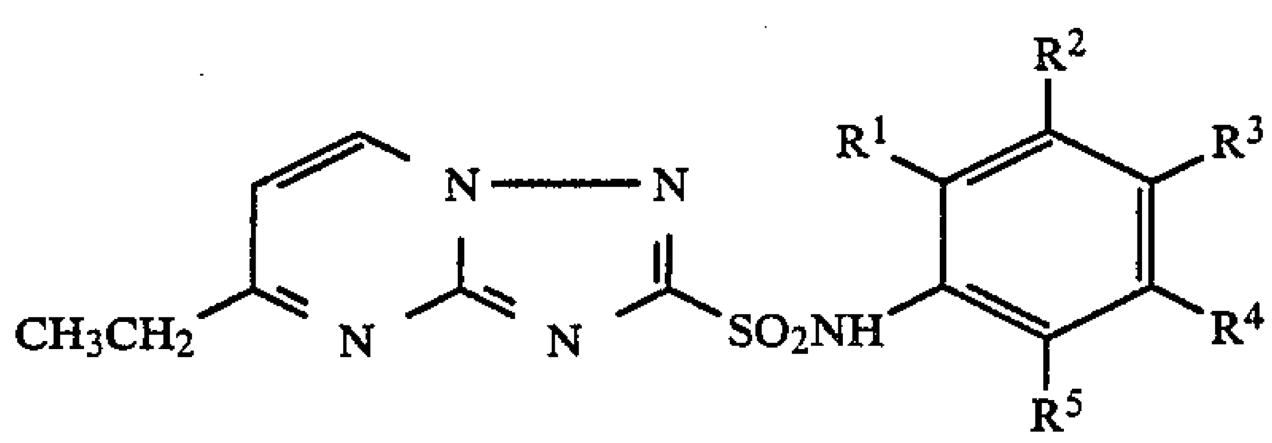
Cmpd.	R1	R2	R3	R4	R5	Melting Point	Elemental Analysis: Analysis	C	H	N
232	Cl	H	H	H	Cl	>310° C.	Calcd. for $C_{12}H_9Cl_2N_5O_3S$:	38.51	2.41	18.72
							Found:	38.28	2.44	19.03

TABLE XXVII



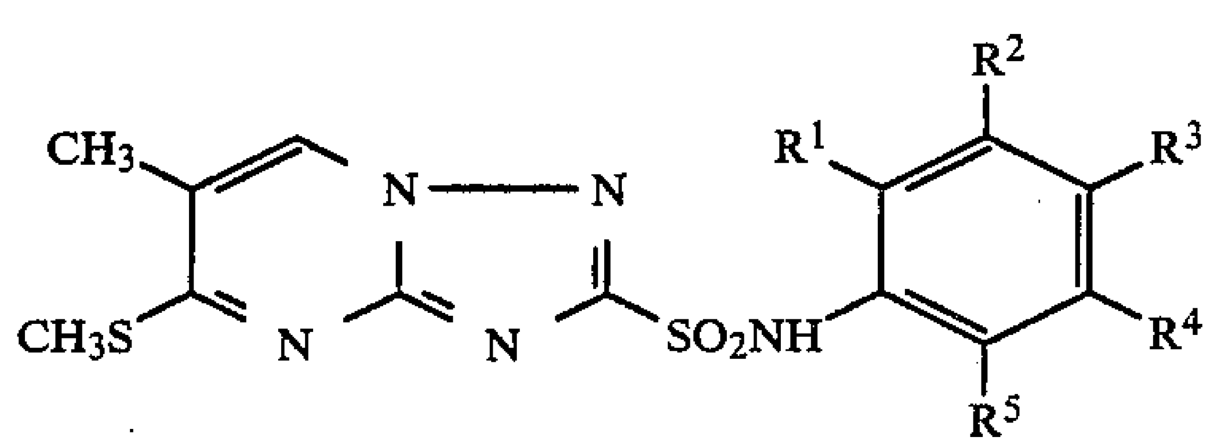
Cmpd.	R[1]	R[2]	R[3]	R[4]	R[5]	Melting Point	Elemental Analysis: Analysis	C	H	N
233	Cl	H	H	H	CH_3	221-224° C.	Calcd. for $C_{15}H_{14}ClN_5O_2S$:	29.52	3.85	19.27
						(decomp.)	Found:	49.56	3.85	18.90

TABLE XXVIII



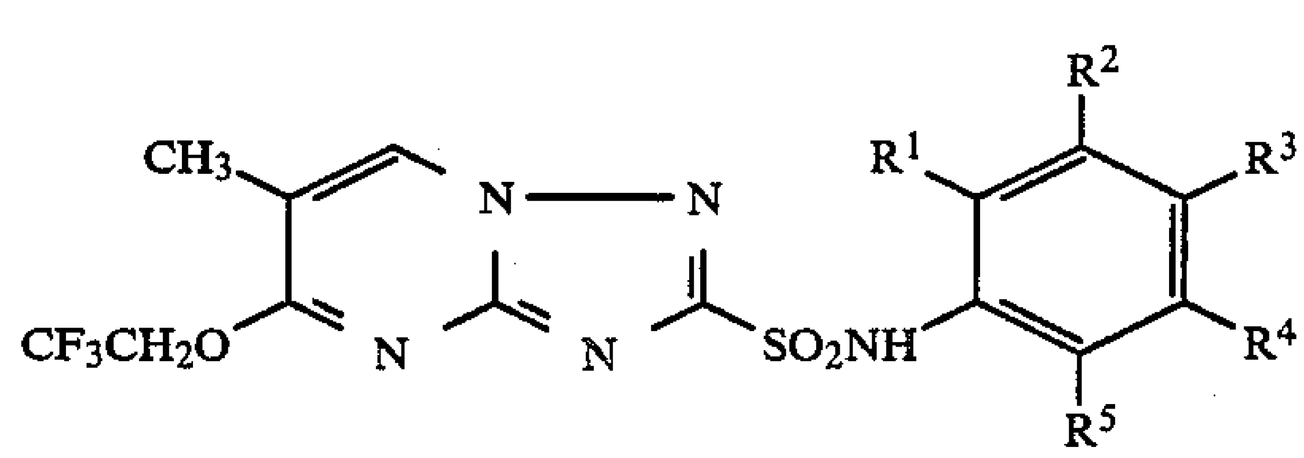
Cmpd.	R[1]	R[2]	R[3]	R[4]	R[5]	Melting Point	Elemental Analysis	
234	Cl	H	H	H	Cl	80-92° C.	Exact mass calcd. for $C_{13}H_{11}Cl_2N_5O_2S$:	327.9981
						(decomp.)	Found:	327.9994

TABLE XXIX



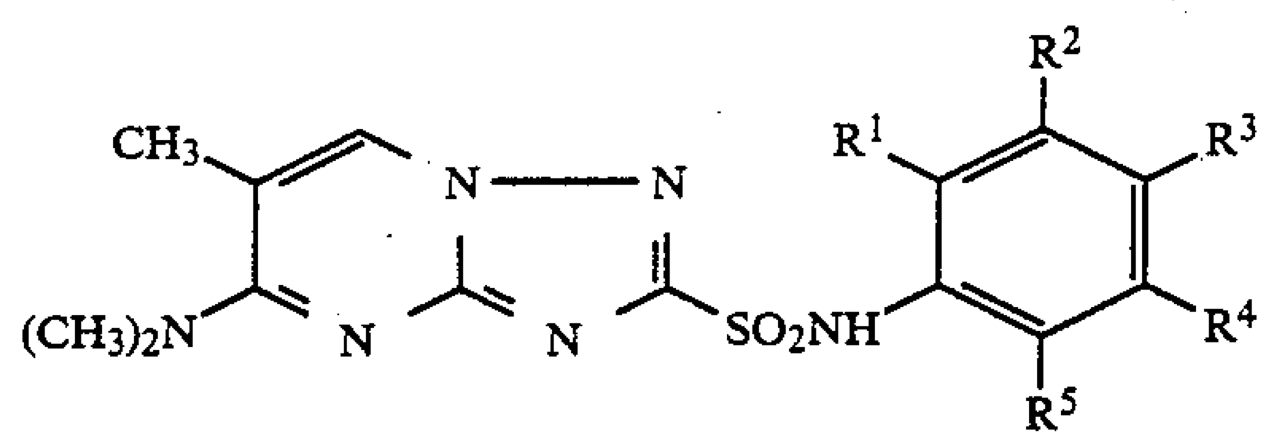
Cmpd.	R[1]	R[2]	R[3]	R[4]	R[5]	Melting Point	Elemental Analysis: Analysis	C	H	N
235	Cl	H	H	H	Cl	254-258° C.	Calcd. for $C_{13}H_{11}Cl_2N_5O_2S_2$:	36.96	2.60	16.58
						(decomp.)	Found:	36.92	2.44	16.57

TABLE XXX



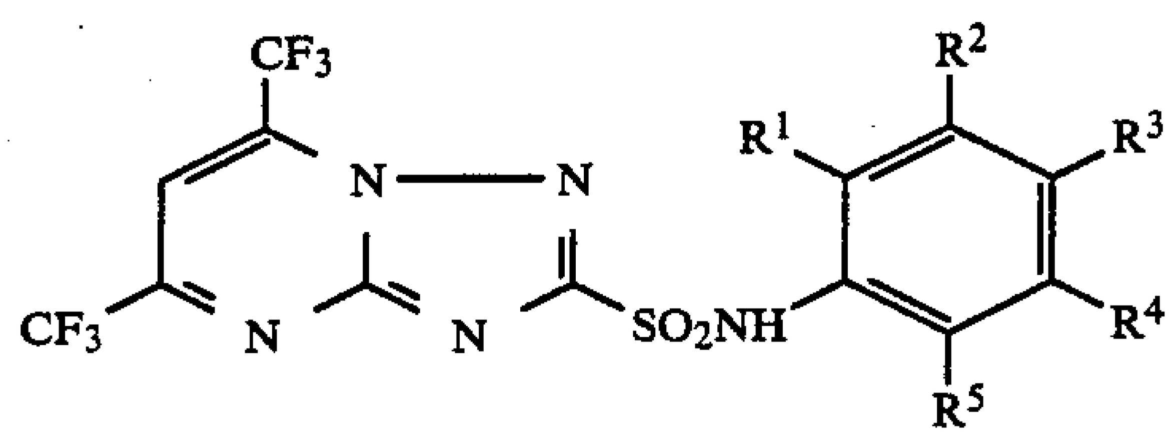
Cmpd.	R[1]	R[2]	R[3]	R[4]	R[5]	Melting Point	Elemental Analysis: Analysis	C	H	N
236	Cl	H	H	H	Cl	250-253° C.	Calcd. for $C_{14}H_{10}Cl_2F_3N_5O_3S$:	36.85	2.19	15.35
						(decomp.)	Found:	36.44	2.07	15.62

TABLE XXXI



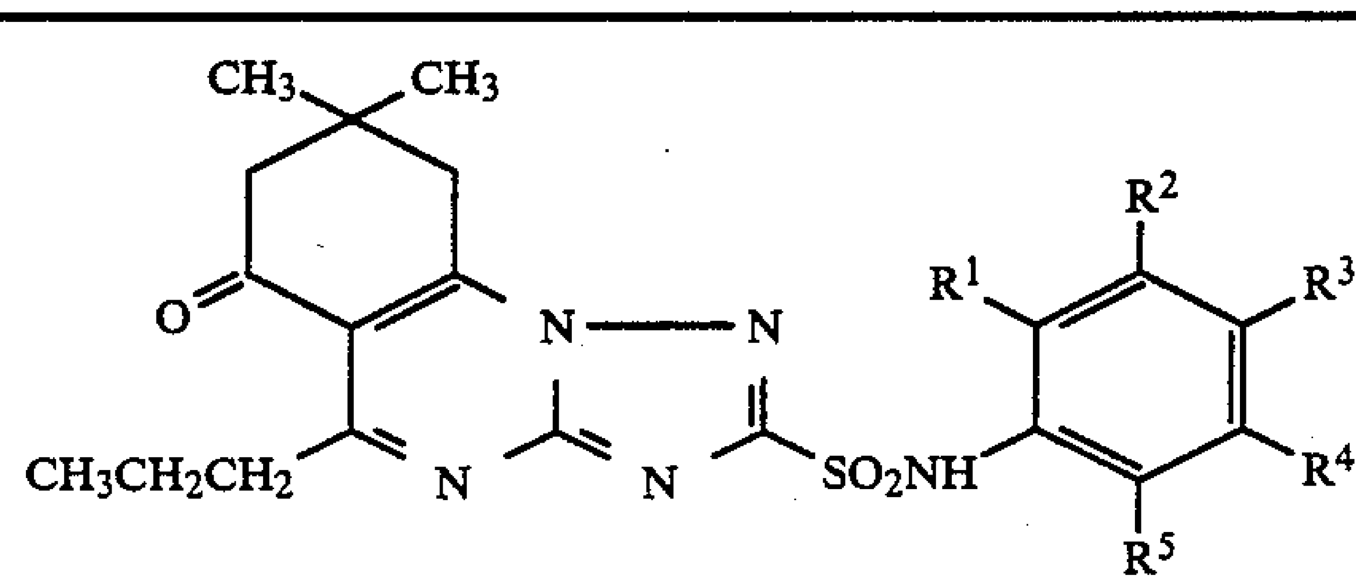
Cmpd.	R^1	R^2	R^3	R^4	R^5	Melting Point	Elemental Analysis: Analysis	C	H	N
237	Cl	H	H	H	Cl	270–274° C. (decomp.)	Calcd. for $C_{14}H_{14}Cl_2N_6O_2S$:	41.89	3.49	20.95
							Found:	41.87	3.49	21.03

TABLE XXXII



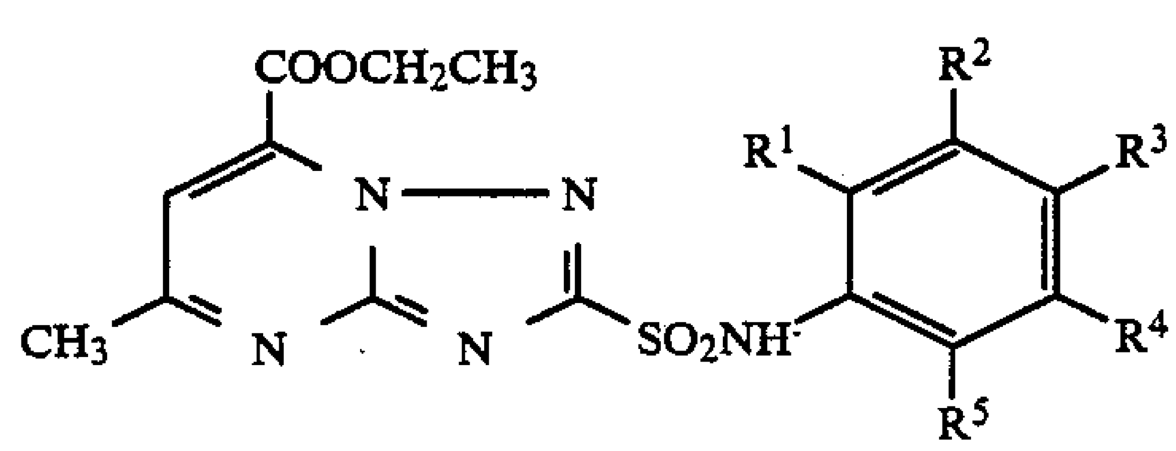
Cmpd.	R^1	R^2	R^3	R^4	R^5	Melting Point	Elemental Analysis: Analysis	C	H	N
238	Cl	H	H	H	Cl	286–287° C.	Calcd. for $C_{13}H_5Cl_2F_6N_5O_2S$:	32.56	1.04	14.59
							Found:	32.98	0.70	14.71

TABLE XXXIII



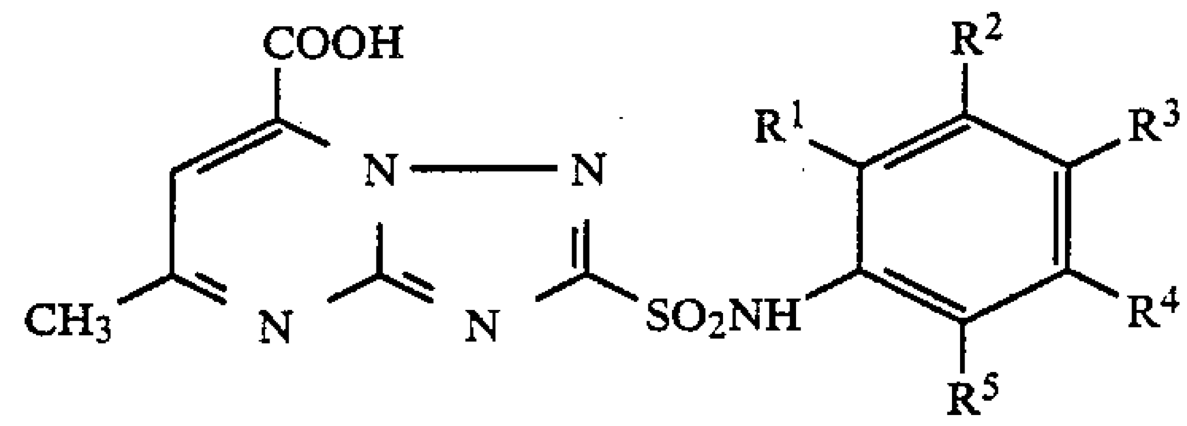
Cmpd.	R^1	R^2	R^3	R^4	R^5	Melting Point	Elemental Analysis: Analysis	C	H	N
239	Cl	H	H	H	Cl	284–286° C.	Calcd. for $C_{20}H_{21}Cl_2N_5O_3S$:	49.90	4.36	14.52
							Found:	49.81	4.22	14.28

TABLE XXXIV



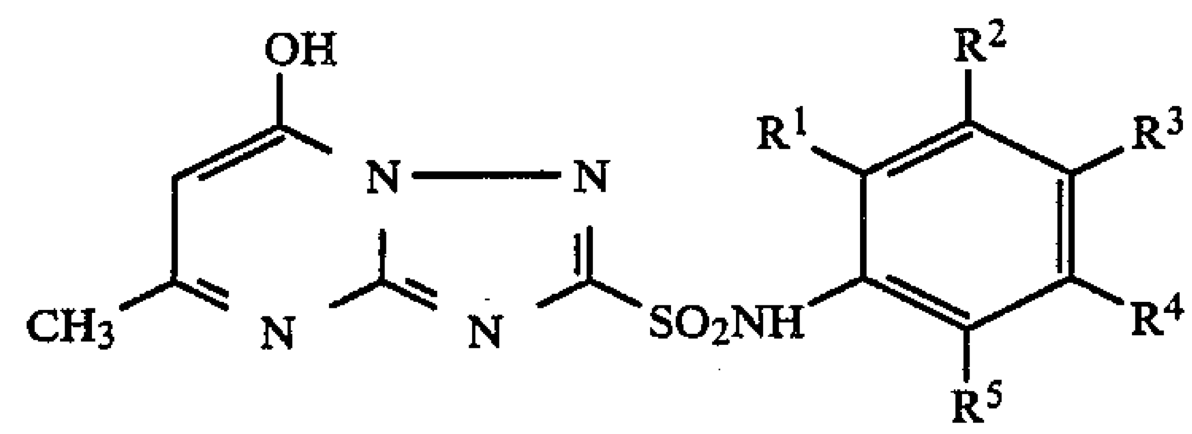
Cmpd.	R^1	R^2	R^3	R^4	R^5	Melting Point	Elemental Analysis: Analysis	C	H	N
240	Cl	H	H	H	Cl	236–239° C. (decomp.)	Calcd. for $C_{15}H_{13}Cl_2N_5O_4S$:	41.86	3.02	16.28
							Found:	41.75	2.79	16.16

TABLE XXXV



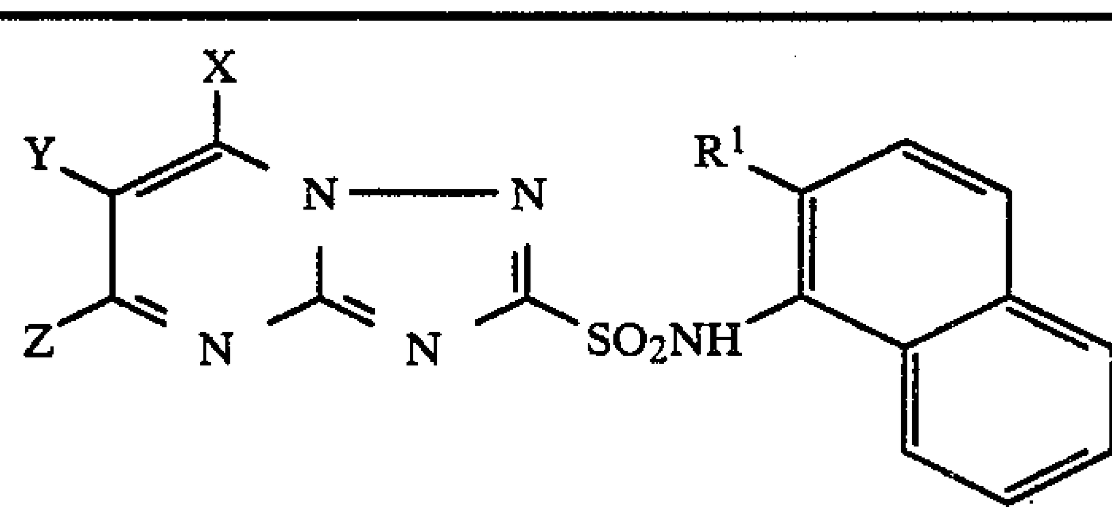
Cmpd.	R^1	R^2	R^3	R^4	R^5	Melting Point	Elemental Analysis: Analysis	C	H	N
241	Cl	H	H	H	Cl	120–130° C. (decomp.)	Calcd. for $C_{13}H_9Cl_2N_5O_4S.H_2O$:	37.15	2.38	16.70
							Found:	37.03	2.02	17.16

TABLE XXXVI



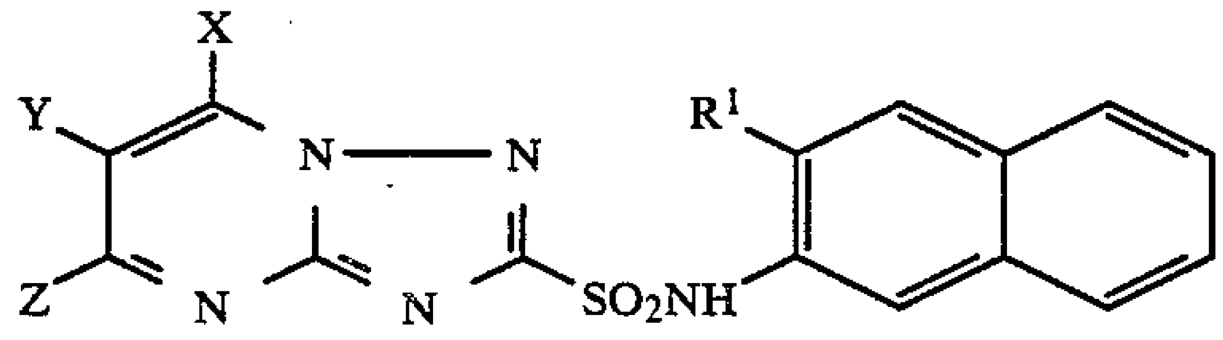
Cmpd.	R^1	R^2	R^3	R^4	R^5	Melting Point	Elemental Analysis: Analysis	C	H	N
242	Cl	H	H	H	Cl	280–304° C. (decomp.)	Calcd. for $C_{12}H_9Cl_2N_5O_3S$:	38.51	2.41	18.72
							Found:	38.52	2.49	19.03
309	F	CH_3	H	H	F	304–305° C.	Calcd. for $C_{13}H_{11}F_2N_5O_3S$:	43.94	3.12	19.71
							Found:	43.86	2.91	19.79
310	CF_3	H	H	H	H	245–247° C.	Calcd. for $C_{13}H_{10}F_3N_5O_3S$:	40.37	3.00	8.29
								40.41	2.76	7.93

TABLE XXXVII



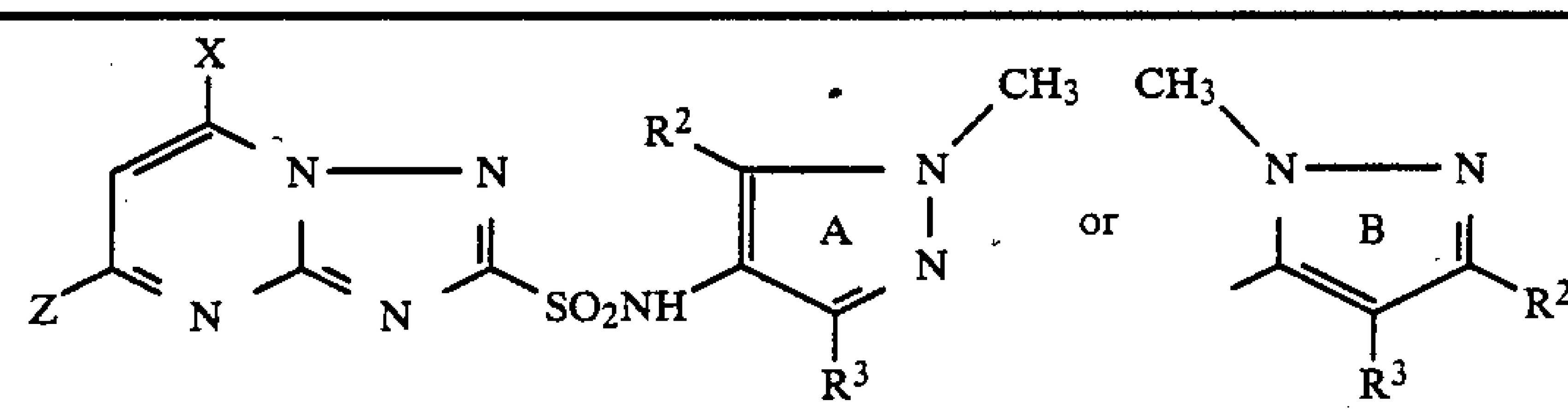
Cmpd.	R^1	X	Y	Z	Melting Point	Elemental Analysis: Analysis	C	H	N
243	Cl	CH_3	H	CH_3	303–306° C. (decomp.)	Calcd. for $C_{17}H_{14}ClN_5O_2S$:	52.65	3.64	18.05
						Found:	52.10	3.65	18.51
244	Cl	H	H	CH_3	262–265° C. (decomp.)	Calcd. for $C_{16}H_{12}ClN_5O_2S$:	51.41	3.24	18.73
						Found:	50.97	3.29	18.99

TABLE XXXVIII



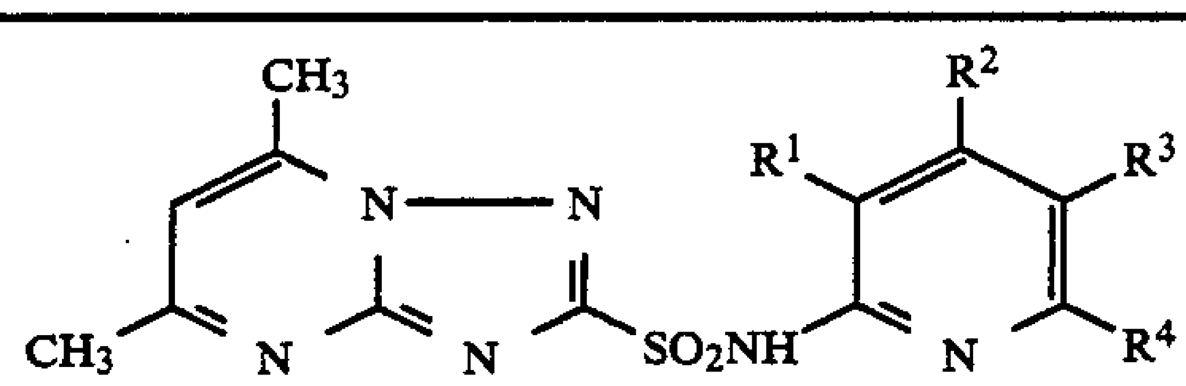
Cmpd.	R^1	X	Y	Z	Melting Point	Elemental Analysis: Analysis	C	H	N
245	COOMe	CH_3	H	CH_3	206–208° C.	Calcd. for $C_{19}H_{17}N_5O_4S.\frac{1}{2}H_2O$:	54.28	4.32	16.65
						Found:	53.98	4.12	16.83

TABLE XXXIX



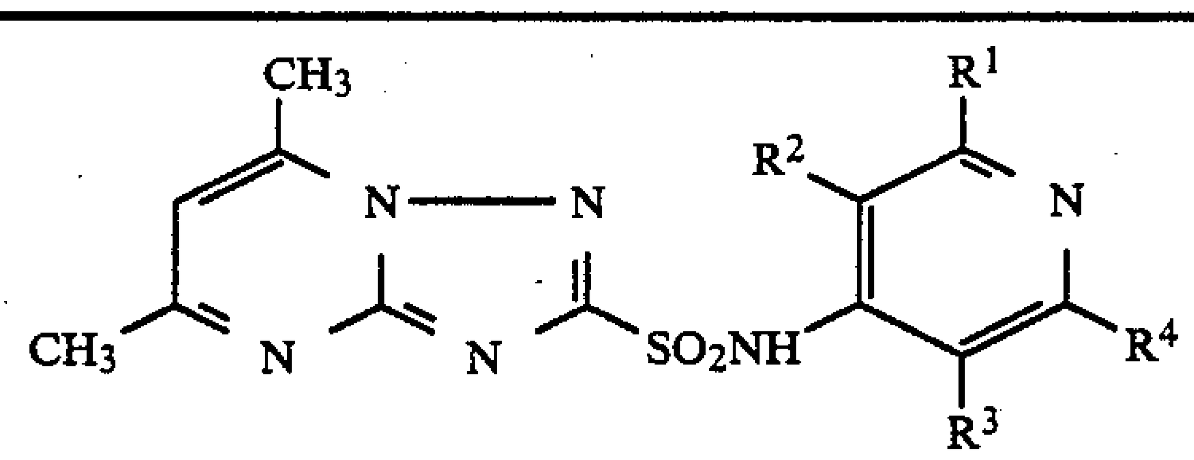
Cmpd.	Pyrazole	R^2	R^3	X	Y	Z	Melting Point	Elemental Analysis: Analysis	C	H	N
246	A	CF_3	CH_3	H		CH_3	273–274° C. (decomp.)	Calcd. for $C_{12}H_{12}F_3N_7O_2S$:	38.39	3.22	26.12
								Found:	38.73	3.23	25.92
247	A	CF_3	CH_3	CH_3		CH_3	288–288.5° C. (decomp.)	Calcd. for $C_{13}H_{14}F_3N_7O_2S$:	40.09	3.62	25.18
								Found:	40.22	3.49	25.17
248	A	COOMe	CH_3	H		CH_3	174–175° C.	Calcd. for $C_{13}H_{15}N_7O_4S$:	42.73	4.14	26.84
								Found:	42.39	4.21	26.91
249	A	H	COOMe	CH_3	CH_3	CH_3	208–210° C.	Calcd. for $C_{14}H_{17}N_7O_4S$:	44.32	4.52	25.85
								Found:	44.07	4.31	25.72
250	A	H	CH_3	COOMe	CH_3	CH_3	228–230° C.	Calcd. for $C_{14}H_{17}N_7O_4S$:	44.32	4.52	25.85
								Found:	44.06	4.82	25.97
311	B	H	COOEt	CH_3	H	CH_3	217–219° C.	Calcd. for $C_{14}H_{17}N_7O_4S$:	44.31	4.52	25.85
								Found:	44.29	4.73	25.63
312	B	CH_3	Br	CH_3	H	CH_3	188° C. (decomp.)	Calcd. for $C_{12}H_{14}BrN_7O_2S$:	36.01	3.53	24.50
								Found:	36.07	3.74	24.27

TABLE XL



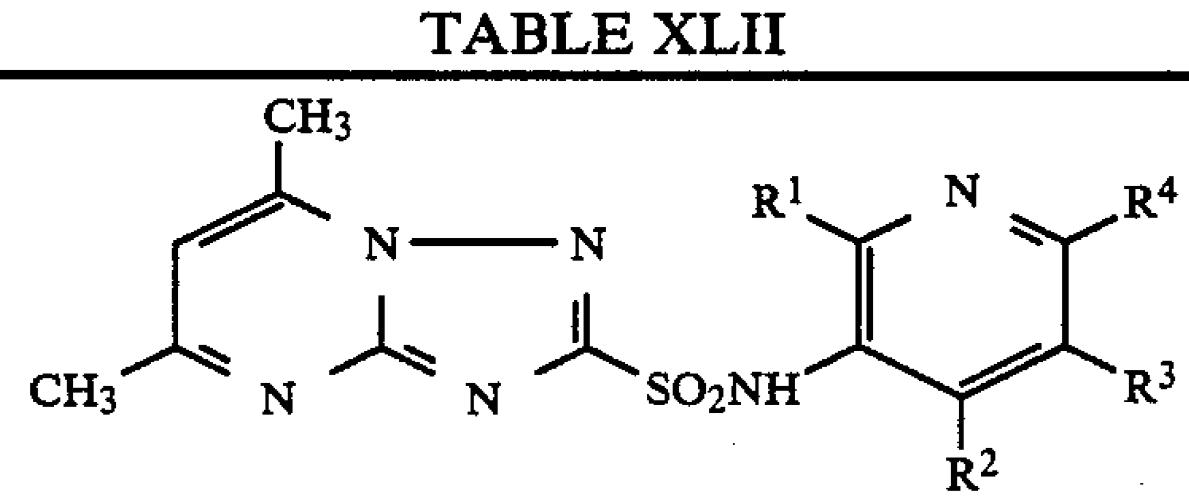
Cmpd.	R^1	R^2	R^3	R^4	Melting Point	Elemental Analysis			
251	Cl	H	Cl	H	159°–161° C.	Exact mass calcd. for $C_{12}H_{10}Cl_2N_6O_2S$:	371.9963		
						Found:	371.9973		
252	Cl	H	H	H	>210° C. (decomp.)	Analysis	C	H	N
						Calcd. for $C_{12}H_{11}ClN_6O_2S$:	42.55	3.27	24.80
						Found:	42.19	3.28	24.27

TABLE XLI



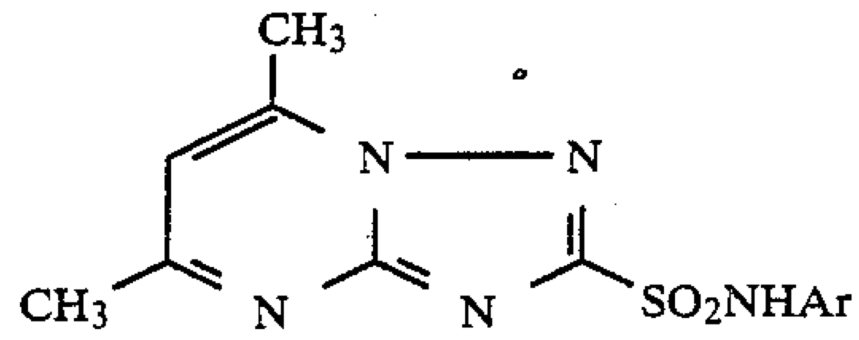
Cmpd.	R^1	R^2	R^3	R^4	Melting Point	Elemental Analysis: Analysis	C	H	N
253	H	H	H	H	>250° C. (decomp.)	Calcd. for $C_{12}H_{12}N_6O_2S.H_2O$:	44.72	4.38	26.06
						Found:	44.88	4.19	26.37
254	H	Cl	H	H	>260° C. (decomp.)	Calcd. for $C_{12}H_{11}ClN_6O_2S$:	42.55	3.27	24.80
						Found:	42.48	3.40	24.49

TABLE XLII



Cmpd.	R^1	R^2	R^3	R^4	Melting Point	Elemental Analysis	
255	Cl	H	H	H	207.5°–208.5° C.	Exact mass calcd. for $C_{12}H_{11}ClN_6O_2S$:	338.0352
						Found:	338.0342

TABLE XLIII



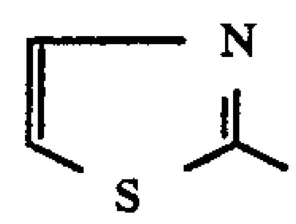
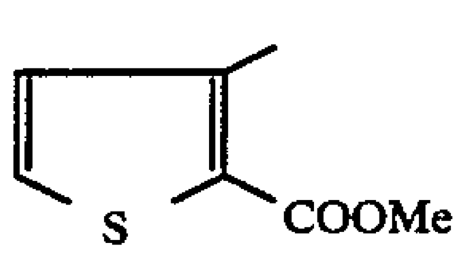
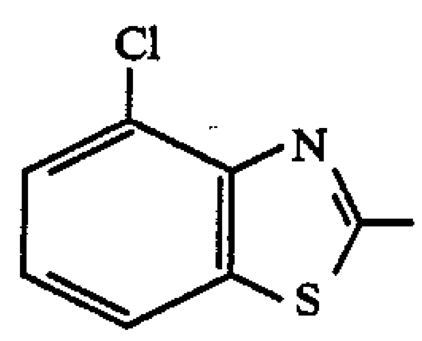
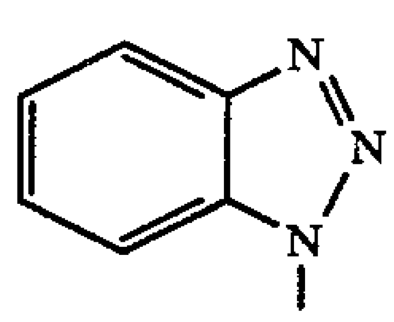
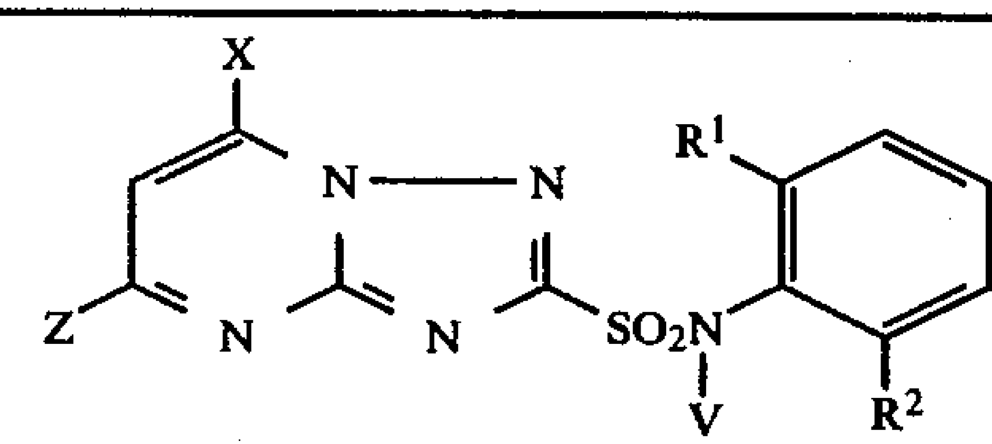
Cmpd.	Ar	Melting Point	Elemental Analysis: Analysis	C	H	N
256		120–125° C.	Calcd. for $C_{10}H_{10}N_6O_2S_2$:	38.66	3.22	27.06
			Found:	38.48	3.28	26.92
257		160–168° C.	Calcd. for $C_{13}H_{13}N_5O_4S_2$:	42.49	3.53	19.05
			Found:	42.04	3.40	18.81
258		224–226° C. (decomp.)	Calcd. for $C_{14}H_{11}ClN_6O_2S_2$:	42.58	2.78	21.27
			Found:	43.10	2.79	20.74
259		195° C. (decomp.)	Calcd. for $C_{13}H_{11}N_8O_2S$:	47.41	3.37	29.78
			Found:	47.01	3.31	30.78

TABLE XLIV



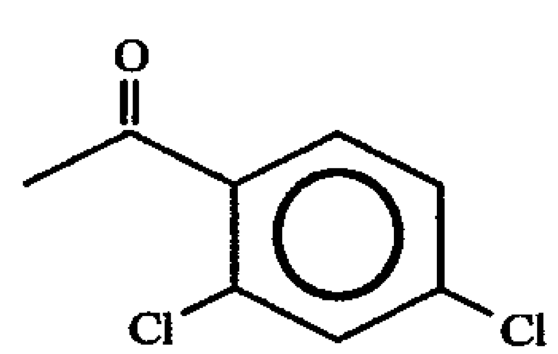
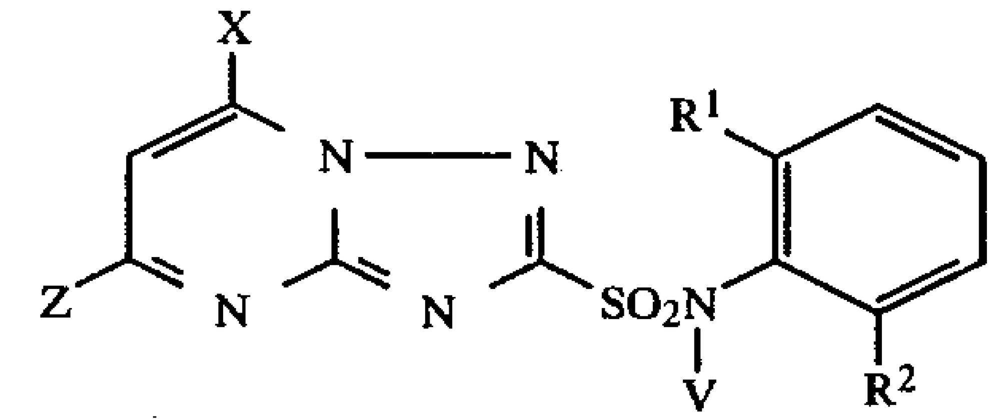
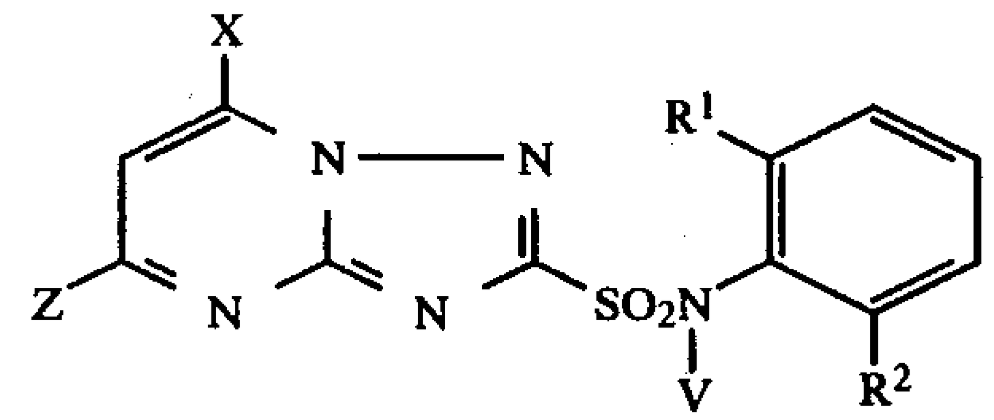
Cmpd.	R^1	R^2	V	X	Z	Melting Point	Analysis	C	H	N	Cl	S
260	Cl	Cl	CH_3	CH_3	CH_3	220–222° C.	Calcd. for $C_{14}H_{13}Cl_2N_5O_2S$:	43.54	3.39	18.13		
							Found:	43.55	3.32	18.03		
261	COOMe	CH_3	CH_3	CH_3	CH_3	175.5–177° C.	Calcd. for $C_{17}H_{19}N_5O_4S$:	52.43	4.92	17.98		
							Found:	52.31	4.93	17.94		
262	Cl	Cl	$COCH_3$	CH_3	CH_3	214–217° C.	Calcd. for $C_{15}H_{13}Cl_2N_5O_3S$:	43.49	3.16	16.90		
							Found:	43.44	3.16	16.77		
263	Cl	Cl	$CH_2CH{=}CH_2$	CH_3	CH_3	182–184° C.	Calcd. for $C_{16}H_{15}Cl_2N_5O_2S$:	46.61	3.67	16.98		
							Found:	46.74	3.67	16.86		
264	Cl	Cl	CH_2COOEt	CH_3	CH_3	173–176° C.	Calcd. for $C_{17}H_{17}Cl_2N_5O_4S$:	44.55	3.74	15.27		
							Found:	44.74	3.74	15.08		
265	Cl	Cl	CH_2Ph	CH_3	CH_3	>240° C. (decomp.)	Calcd. for $C_{20}H_{17}Cl_2N_5O_2S.\frac{1}{2}H_2O$:	50.97	3.85	14.85		
							Found:	50.93	3.66	14.85		
266	COOMe	CH_3	CH_2COOEt	CH_3	CH_3	152–155° C.	Calcd. for $C_{20}H_{23}N_5O_6S$:	52.05	5.02	15.17		
							Found:	51.64	4.94	15.39		
267	COOMe	CH_3	CH_2Ph	CH_3	CH_3	174–176° C.	Calcd. for $C_{23}H_{23}N_5O_4S$:	59.34	4.98	15.04		
							Found:	59.00	4.89	15.18		
268	Cl	Cl	$COCH_3$	H	CH_3	176–181° C.	Calcd. for $C_{14}H_{11}Cl_2N_5O_3S$:	42.02	2.77	17.49		
							Found:	42.28	2.90	17.16		
269	Cl	Cl	CoiPr	H	CH_3	193–194.5° C.	Calcd. for $C_{16}H_{15}Cl_2N_5O_3S$:	44.87	3.53	16.35		
							Found:	45.26	3.53	16.39		
270	Cl	Cl	$COC_{11}H_{23}$		CH_3	105.5–106.5° C.	Calcd. for $C_{24}H_{31}Cl_2N_5O_3S$:	53.33	5.78	12.96		
							Found:	53.40	5.77	12.84		
271	Cl	Cl		H	CH_3	234–235° C.	Calcd. for $C_{19}H_{11}Cl_4N_5O_3S$:	42.96	2.09	13.18		
							Found:	43.31	2.29	13.04		
272	Cl	Cl	CO_2Et	H	CH_3	189–191° C.	Calcd. for $C_{15}H_{15}Cl_2N_5O_4S$:	41.87	3.05	16.28		
							Found:	42.51	3.25	16.02		
273	Cl	Cl	$CON(CH_3)_2$	H	CH_3	225–228° C. (decomp.)	Calcd. for $C_{15}H_{14}Cl_2N_6O_3S$:	41.97	3.29	19.58		
							Found:	42.08	3.27	20.18		
274	Cl	Cl	COPh	H	CH_3	187–189° C.	Calcd. for $C_{19}H_{13}Cl_2N_5O_3S$:	49.36	2.83	15.15		
							Found:	48.97	2.84	15.16		
275	F	F	$COCH_3$	H	CH_3	195–200° C.	Calcd. for $C_{14}H_{11}F_2N_5O_3S$:	45.77	3.02	19.07		8.73
							Found:	45.59	3.12	19.16		8.91
276	F	F	COEt	H	CH_3	154–160° C.	Calcd. for $C_{15}H_{13}F_2N_5O_3S$:	47.24	3.44	18.37		8.41
							Found:	47.05	3.44	18.49		8.27
277	F	F	COiPr	H	CH_3	182–184° C.	Calcd. for $C_{16}H_{15}F_2N_5O_3S$:	48.60	3.82	17.71		

TABLE XLIV-continued



Cmpd.	R^1	R^2	V	X	Z	Melting Point	Analysis	Elemental Analysis C	H	N	Cl	S
							Found:	48.41	3.93	17.43		
278	F	F	$COCH_2tBu$	H	CH_3	158–162° C.	Calcd. for $C_{18}H_{19}F_2N_5O_3S$:	51.05	4.52	16.54		7.57
							Found:	51.15	4.62	16.38		7.83
279	F	F	COnBu	H	CH_3	131–134° C.	Calcd. for $C_{17}H_{17}F_2N_5O_3S$:	49.87	4.19	17.11		
							Found:	49.10	4.04	17.05		
280	F	F	COtBu	H	CH_3	185–186° C.	Calcd. for $C_{17}H_{17}F_2N_5O_3S$:	49.87	4.19	17.11		7.83
						(decomp.)	Found:	49.93	3.89	16.82		7.10
281	F	F	$COCH_2Ph$	H	CH_3	178–185° C.	Calcd. for $C_{20}H_{15}F_2N_5O_3S$:	54.17	3.41	15.80		
							Found:	53.60	3.18	15.56		
282	F	F	$COCH_2CH_2Cl$	H	CH_3	195° C.	Calcd. for $C_{15}H_{12}ClF_2N_5O_3S$:	43.33	2.91	16.84	8.53	7.71
						(decomp.)	Found:	43.21	2.95	17.31	8.45	7.47
283	F	F	COnPr	H	CH_3	130–135° C.	Calcd. for $C_{16}H_{15}F_2N_5O_3S$:	48.60	3.82	17.71		8.11
							Found	48.42	3.81	17.91		7.98
284	F	F	$COCH_2iPr$	H	CH_3	154–159° C.	Calcd. for $C_{17}H_{17}F_2N_5O_3S$:	49.87	4.19	17.11		7.83
							Found	49.45	4.04	17.15		7.68
285	F	F	$COCH_2Cl$	H	CH_3	156–158° C.	Calcd. for $C_{14}H_{10}ClF_2N_5O_3S$:	41.85	2.51	17.43		
							Found:	42.19	2.68	17.43		
286	F	F	$COCHCH_3{=}CH_2$	H	CH_3	171.5–174° C.	Calcd. for $C_{16}H_{13}F_2N_5O_3S$:	48.85	3.33	17.81		8.15
							Found	48.36	3.51	17.91		7.94
287	F	F	$COnC_9H_{19}$	H	CH_3	97–99° C.	Calcd. for $C_{22}H_{27}F_2N_5O_3S$:	55.10	5.68	14.61		6.69
							Found	55.22	5.60	14.85		6.63
288	F	F	$COCH{=}CHCH_3$	H	CH_3	154–156° C.	Calcd. for $C_{16}H_{13}F_2N_5O_3S$:	48.85	3.33	17.81	8.15	
							Found:	48.41	3.41	17.94	8.49	
289	F	F	$COcycloC_3H_5$	H	CH_3	200.5–203° C.	Calcd. for $C_{16}H_{13}F_2N_5O_3S$:	48.85	3.33	17.81		8.15
							Found:	48.32	3.34	18.03		8.34
290	F	F	COPh	H	CH_3	186–189° C.	Calcd. for $C_{19}H_{13}F_2N_5O_3S$:	53.14	3.05	16.31		7.47
							Found:	53.74	3.16	16.63		7.11
291	F	F	$COcycloC_6H_{11}$	H	CH_3	178–180° C.	Calcd. for $C_{19}H_{19}F_2N_5O_3S$:	52.40	4.40	16.08		7.36
							Found:	51.40	4.28	16.08		7.78
292	F	F	$COCH_2OPh$	H	CH_3	141–144° C.	Calcd. for $C_{20}H_{15}F_2N_5O_4S$:	52.28	3.29	15.25		6.98
							Found:	51.77	3.38	15.28		6.76
293	F	F	$COCH{=}CHPh$	H	CH_3	oil	Calcd. for $C_{21}H_{15}F_2N_5O_3S$:	55.38	3.32	15.38		7.04
							Found:	55.55	3.45	15.29		6.98
294	F	F	$COCH_2CH_2{-}CO_2CH_2CH_3$	H	CH_3	157–162° C.	Calcd. for $C_{18}H_{17}F_2N_5O_5S$:	47.68	3.78	15.45		7.07
							Found:	47.32	3.78	15.68		7.03
295	F	F	CO(2-furyl)	H	CH_3	120° C.	Calcd. for $C_{17}H_{11}F_2N_5O_4S$:	48.69	2.64	16.70		7.65
						(decomp.)	Found:	48.49	2.75	17.03		7.83
296	F	F	$COcycloC_4H_7$	H	CH_3	161–170° C.	Calcd. for $C_{17}H_{15}F_2N_5O_3S$:	50.12	3.71	17.19		7.87
							Found:	49.58	3.89	17.21		8.07
297	F	F	SO_2CH_3	H	CH_3	193–195° C.	Calcd. for $C_{13}H_{11}F_2N_5O_4S_2$:	38.71	2.75	17.36		15.90
							Found:	38.98	2.92	17.18		15.72
298	F	F	SO_2Ph	H	CH_3	182–190° C.	Calcd. for $C_{18}H_{13}F_2N_5O_4S_2$:	46.45	2.82	15.05		13.78

TABLE XLIV-continued



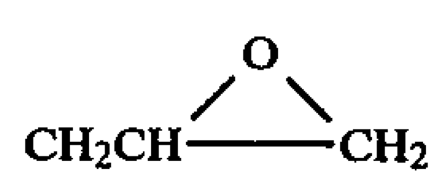
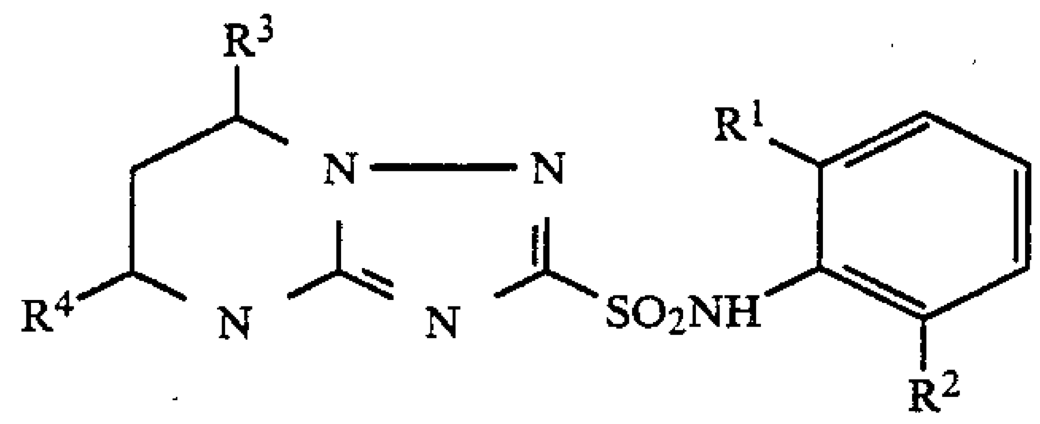
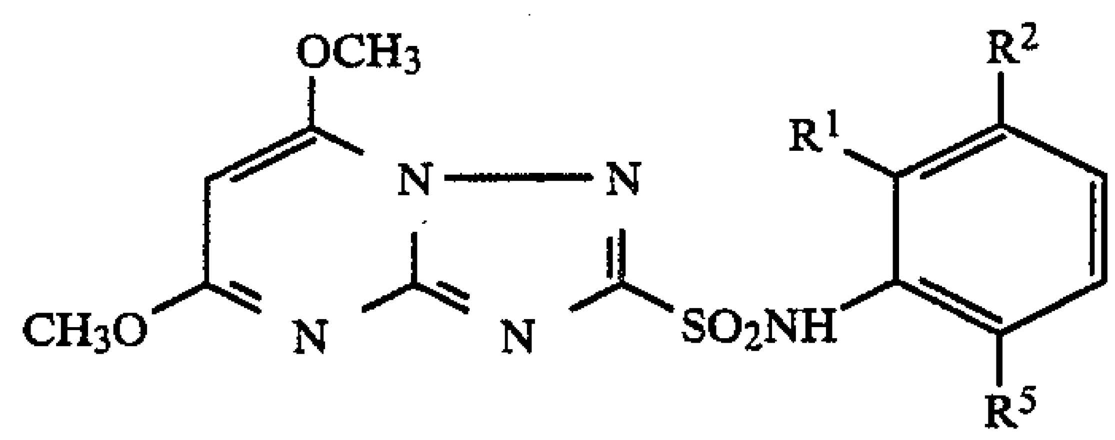
Cmpd.	R^1	R^2	V	X	Z	Melting Point	Analysis	Elemental Analysis C	H	N	Cl	S
							Found:	46.41	3.03	14.79		14.01
299	F	F	CH_2Ph	H	CH_3	170–177° C.	Calcd. for $C_9H_{15}F_2N_5O_2S$:	54.93	3.64	16.86		7.72
							Found	54.45	3.73	16.63		7.77
300	F	F	C=O(SEt)	H	CH_3	197–199° C.	Calcd. for $C_{15}H_{13}F_2N_5O_3S_2$:	43.58	3.17	16.94		15.51
							Found:	43.45	3.19	17.12		15.64
301	F	F	$CH_2(4\text{-}NO_2Ph)$	H	CH_3	194–200° C.	Calcd. for $C_{19}H_{14}F_2N_6O_4S$:	49.64	3.07	18.26		6.96
							Found	49.64	3.25	18.40		6.88
302	F	F	CH_2(4-MeOPh)	H	CH_3	156–158° C.	Calcd. for $C_{20}H_{17}F_2N_5O_3S$:	53.92	3.85	15.72		7.20
							Found	53.65	3.98	15.95		7.46
303	F	F	CH_2(2-furyl)	H	CH_3	177–180° C.	Calcd. for $C_{17}H_{13}F_2N_5O_3S$:	50.37	3.23	17.28		7.91
							Found:	50.50	3.30	17.33		7.74
313	F	F	CH_2SCH_3	H	CH_3	195–200° C.	Calcd. for $C_{14}H_{13}F_2N_5O_2S_2$:	43.63	3.40	18.16		
							Found:	44.04	3.53	18.37		
314	F	F		H	CH_3	132–135° C.	Calcd. for $C_{15}H_{13}F_2N_5O_3S$:	47.24	3.44	18.36		
							Found:	47.15	3.58	18.11		
315	F	F	$CH_2OCH_2CH_2OCH_3$	H	CH_3	127–131° C.	Calcd. for $C_{16}H_{17}F_2N_5O_4S$:	46.49	4.15	16.93		
							Found:	46.40	4.17	17.11		
316	F	F	$(CH_2)_4COOCH_2CH_3$	H	CH_3	96–100° C.	Calcd. for $C_{19}H_{21}F_2N_5O_4S$:	50.33	4.67	15.44		
							Found:	49.70	4.61	15.57		

TABLE XLV



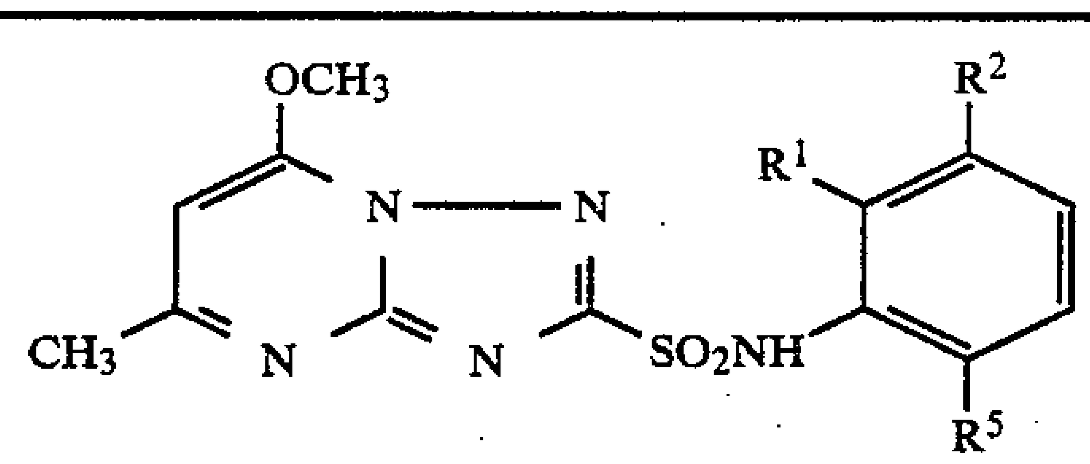
Cmpd.	R^1	R^2	R^3	R^4	Melting Point	Elemental Analysis			
						Analysis	C	H	N
304	Cl	Cl	Me	Me	198–205° C.	Calcd. for $C_{13}H_{15}Cl_2N_5O_2S$:	41.49	3.98	18.50
						Found:	41.27	3.81	18.28
305	CF_3	H	Me	Me	74.5–84° C.	Exact mass calcd. for $C_{14}H_{16}F_3N_5O_2S$:			375.0979
						Found:			375.0978
						Analysis	C	H	N
306	Cl	Cl	H	Me	230–235° C.	Calcd. for $C_{12}H_{13}Cl_2N_5O_2S$:	39.89	3.32	19.39
						Found:	39.72	3.42	19.90

TABLE XLVI



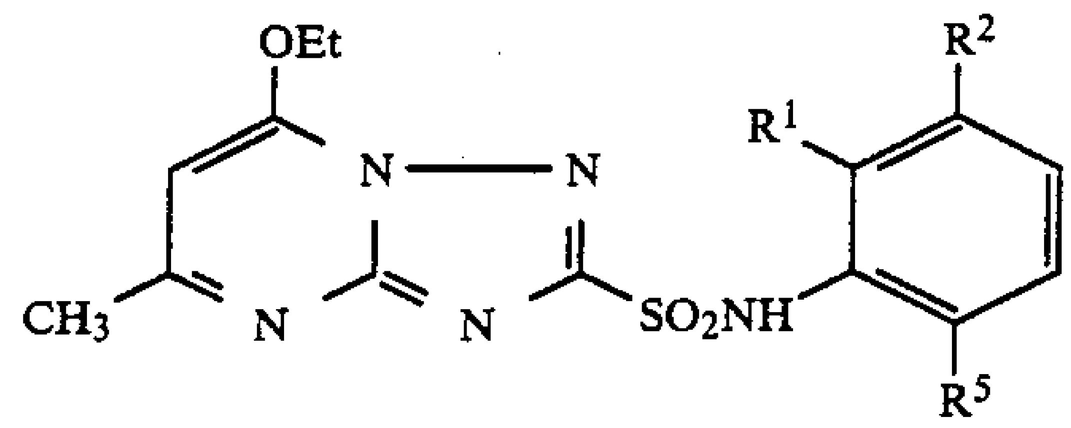
Cmpd.	R^1	R^2	R^5	Melting Point	Analysis	C	H	N
					Elemental Analysis			
317	Cl	H	Cl	232–234° C. (decomp.)	Calcd. for $C_{13}H_{11}Cl_2N_5O_4S$:	38.62	2.74	17.30
					Found:	38.39	2.83	16.70
318	CF_3	H	OCH_3	205–210° C. (decomp.)	Calcd. for $C_{15}H_{14}F_3N_5O_5S$:	41.57	3.26	16.16
					Found:	41.19	3.27	15.98
319	Cl	CH_3	Cl	206–208° C. (decomp.)	Calcd. for $C_{14}H_{13}CL_2N_5O_4S$:	40.20	3.13	16.75
					Found:	39.89	3.09	16.58
320	F	H	Cl	229–230° C. (decomp.)	Calcd. for $C_{13}H_{11}ClFN_5O_4S$:	40.26	2.86	18.06
					Found:	39.87	2.86	17.83
321	Br	H	Cl	231–233° C. (decomp.)	Calcd. for $C_{13}H_{11}BrClN_5O_4S$:	34.80	2.47	15.61
					Found:	34.41	2.02	15.48
322	Cl	H	CH_3	204–206° C. (decomp.)	Calcd. for $C_{14}H_{14}ClN_5O_4S$:	43.81	3.68	18.25
					Found:	43.62	3.63	18.38

TABLE XLVII



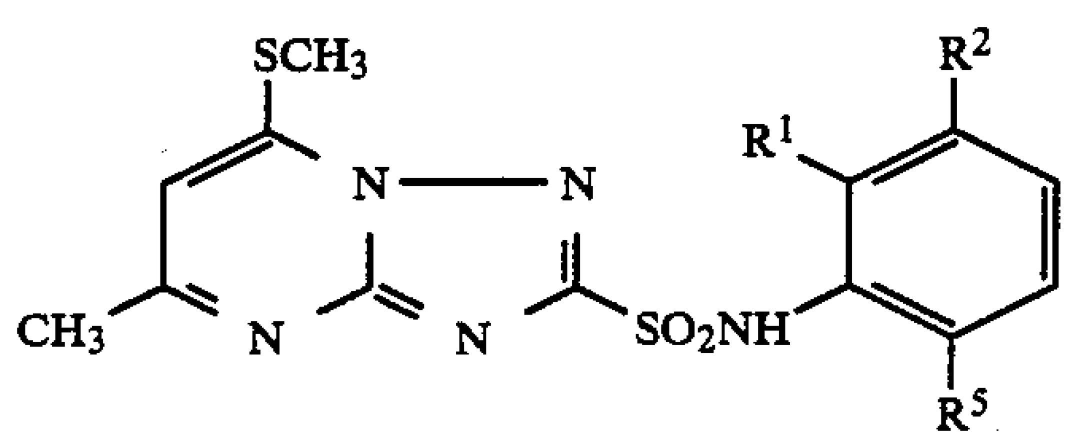
Cmpd.	R^1	R^2	R^5	Melting Point	Analysis	C	H	N	S
					Elemental Analysis				
323	Cl	H	Cl	214–215° C. (decomp.)	Calcd. for $C_{13}H_{11}Cl_2N_5O_3S$:	40.21	2.84	18.04	
					Found:	39.84	3.08	17.99	
324	CF_3	H	OCH_3	205–210° C. (decomp.)	Calcd. for $C_{15}H_{14}F_3N_5O_4S$:	43.16	3.38	16.78	
					Found:	42.92	3.44	16.88	
325	Cl	CH_3	Cl	239–242° C. (decomp.)	Calcd. for $C_{14}H_{13}Cl_2N_5O_3S$:	41.80	3.26	17.41	7.97
					Found:	41.35	3.19	17.42	8.15
326	Cl	H	F	246–247° C. (decomp.)	Calcd. for $C_{13}H_{11}ClFN_5O_3S$:	42.00	2.98	18.84	
					Found:	41.63	3.10	18.57	
327	CF_3	H	H	181–183° C. (decomp.)	Calcd. for $C_{14}H_{12}F_3N_5O_3S$:	43.41	3.12	18.08	8.28
					Found:	43.20	3.13	17.88	8.18
328	F	H	F	226–235° C. (decomp.)	Calcd. for $C_{13}H_{11}F_2N_5O_3S$:	43.94	3.12	19.71	9.02
					Found:	43.50	3.09	19.32	8.81

TABLE XLVIII



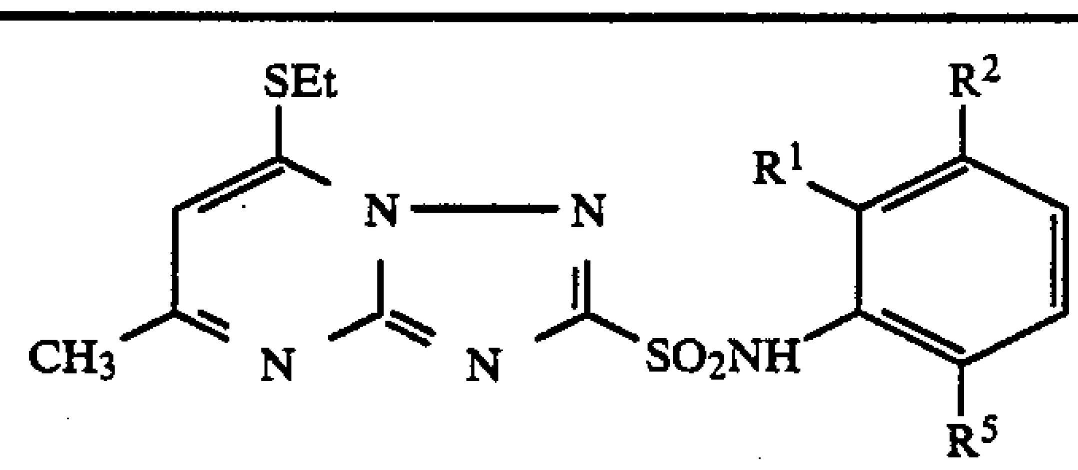
Cmpd.	R¹	R²	R⁵	Melting Point	Elemental Analysis: Analysis	C	H	N	S
329	Cl	H	Cl	222–225° C.	Calcd. for $C_{14}H_{13}Cl_2N_5O_3S$:	41.80	3.26	17.41	7.97
					Found:	41.56	3.37	17.24	7.76
330	CF_3	H	OCH_3	210–213° C.	Calcd. for $C_{16}H_{16}F_3N_5O_4S$:	44.54	3.74	16.24	7.43
					Found:	43.89	3.68	16.00	7.70
331	Cl	CH_3	Cl	228–229° C.	Calcd. for $C_{15}H_{15}Cl_2N_5O_3S$:	43.28	3.63	16.83	7.70
					Found:	42.87	3.66	16.92	7.66
332	Cl	H	F	211–212° C.	Calcd. for $C_{14}H_{13}ClFN_5O_3S$:	43.58	3.40	18.15	
					Found:	43.36	3.41	18.01	
333	CF_3	H	H	187–188° C.	Calcd. for $C_{15}H_{14}F_3N_5O_3S$:	44.88	3.52	17.45	7.99
					Found:	44.67	3.49	17.48	8.10
334	F	H	H	208.5–210.5° C.	Calcd. for $C_{14}H_{13}F_2N_5O_3S$:	45.52	3.55	18.96	8.68
					Found:	45.28	3.56	19.31	8.60
335	F	CH_3	F	192–195° C.	Calcd. for $C_{15}H_{15}F_2N_5O_3S$:	46.99	3.94	18.27	8.36
					Found:	46.76	3.96	18.10	8.19

TABLE XLIX



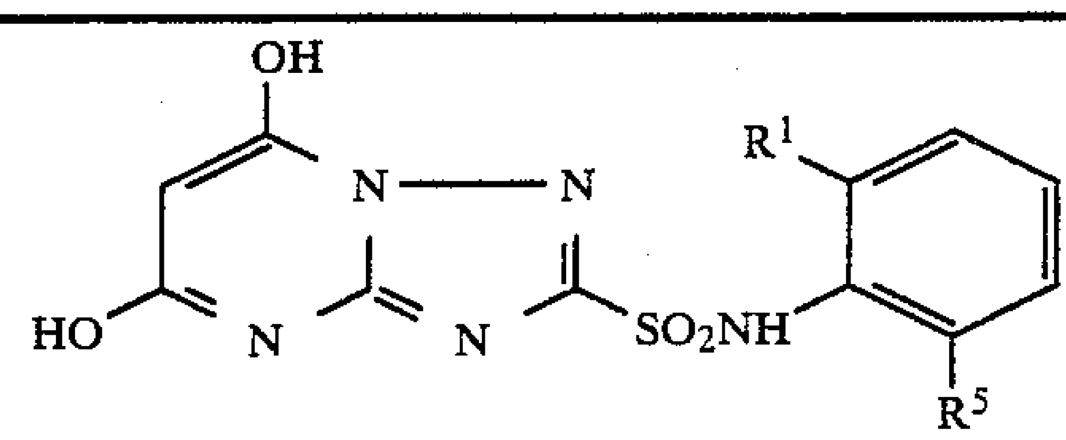
Cmpd.	R¹	R²	R⁵	Melting Point	Elemental Analysis: Analysis	C	H	N	S
336	Cl	H	Cl	300–304° C.	Calcd. for $C_{13}H_{11}Cl_2N_5O_2S_2$:	38.61	2.72	17.32	
				(decomp.)	Found:	38.99	2.93	17.34	
337	CF_3	H	OCH_3	245–249° C.	Calcd. for $C_{15}H_{14}F_3O_3S_2$:	41.56	3.26	16.16	
				(decomp.)	Found:	41.42	3.25	16.30	
338	CF_3	H	H	193–200° C.	Calcd. for $C_{14}H_{12}F_3N_5O_2S_2$:	41.68	3.00	17.36	15.90
					Found:	41.39	2.95	17.21	15.65
339	NO_2	H	CH_3	266–267° C.	Calcd. for $C_{14}H_{14}N_6O_4S_2$:	42.63	3.58	21.31	16.26
					Found:	42.32	3.64	21.46	15.98

TABLE L



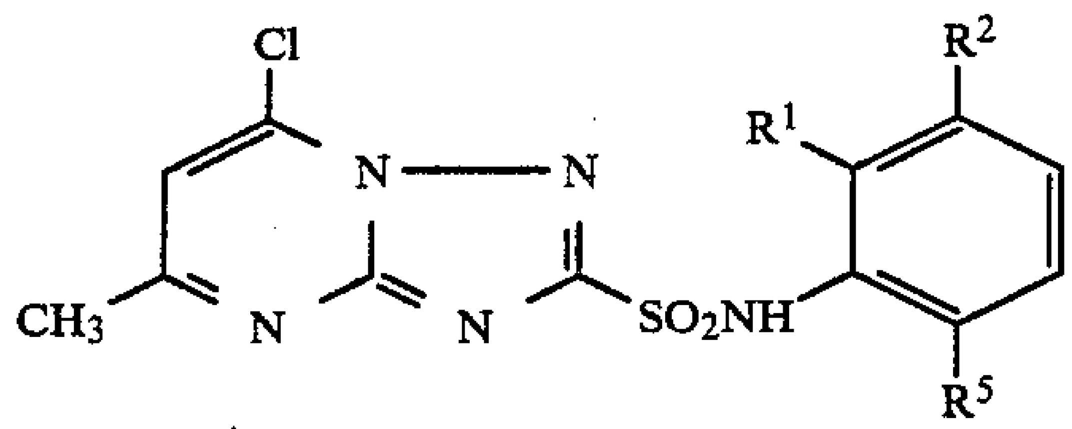
Cmpd.	R¹	R²	R⁵	Melting Point	Elemental Analysis: Analysis	C	H	N	S
340	CF_3	H	OCH_3	228–235° C.	Calcd. for $C_{16}H_{16}N_5O_3S_2$:	42.95	3.60	15.65	
					Found:	42.55	3.53	15.53	
341	CF_3	H	H	202–202.5° C.	Calcd. for $C_{15}H_{14}F_3N_5O_2S_2$:	43.16	3.38	16.78	15.36
					Found:	43.09	3.42	16.69	15.41
342	Cl	H	CH_3	231–233° C.	Calcd. for $C_{15}H_{16}ClN_5O_2S_2$:	45.16	4.04	17.56	16.07
					Found:	45.31	4.10	17.44	16.17
343	F	CH_3	F	233–235° C.	Calcd. for $C_{15}H_{15}F_2N_5O_2S_2$:	45.16	3.78	17.52	16.03
					Found:	44.77	3.89	17.14	16.42

TABLE LI



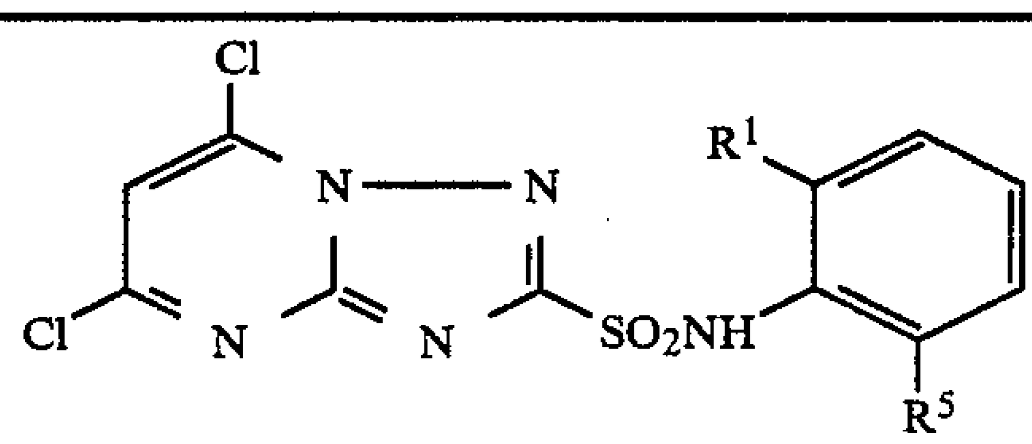
Cmpd.	R^1	R^5	Melting Point	Analysis	C	H	N	Cl	S
				Elemental Analysis					
344	Cl	Cl	306–308° C. (decomp.)	Calcd. for $C_{11}H_7ClN_5O_4S.H_2O$:	39.90	3.35	16.60		
				Found:	40.36	3.32	16.08		
345	F	Cl	240–242° C. (decomp.)	Calcd. for $C_{11}H_7ClFN_5O_4S.H_2O$:	34.98	2.40	18.54		
				Found:	33.87	2.36	18.01		
346	Br	Cl	200–203° C. (decomp.)	Calcd. for $C_{11}H_7ClBrN_5O_4S.H_2O$:	30.12	2.07	15.97		
				Found:	28.65	2.09	16.21		
347	Cl	CH_3	>250° C. (decomp.)	Calcd. for $C_{12}H_{10}ClN_5O_4S.H_2O$:	38.56	3.24	18.74	9.29	8.58
				Found	38.13	2.97	18.32	9.58	8.54

TABLE LII



Cmpd.	R^1	R^2	R^5	Melting Point	Analysis	C	H	N	S
					Elemental Analysis				
348	Cl	H	Cl	217–221° C.	Calcd. for $C_{12}H_8Cl_3N_5O_2S$:	36.70	2.04	17.84	
					Found:	36.69	2.13	17.93	
349	CF_3	H	OCH_2CH_3	212° C. (decomp.)	Calcd. for $C_{15}H_{13}ClF_3N_5O_3S$:	41.34	3.01	16.07	
					Found:	41.14	3.21	16.41	
350	F	CH_3	F	185–187° C. (decomp.)	Calcd. for $C_{13}H_{10}ClF_2N_5O_2S.H_2O$:	39.85	3.09	17.88	8.18
					Found:	39.98	2.87	17.52	8.02

TABLE LIII



Cmpd.	R^1	R^5	Melting Point	Analysis	C	H	N
				Elemental Analysis			
351	Cl	Cl	184–210° C. (decomp.)	Calcd. for $C_{11}H_5Cl_4N_5O_2S$:	31.98	1.22	16.96
				Found:	31.54	1.70	17.41
352	Cl	CH_3	222–224° C.	Calcd. for $C_{12}H_8Cl_3N_5O_2S$:	36.71	2.05	17.84
				Found:	37.05	2.04	17.73

The compounds of the present invention are highly effective herbicides when applied to the locus of vegetation, herein defined as encompassing pre-emergent (soil) applications as well as post-emergent (foliar) applications. They have utility for broad spectrum pre- and/or post-emergence weed control in areas where complete vegetation control is desired. Certain of these compounds are effective for the control of nutsedge (cyperus spp.). The subject compounds are also useful for selective pre- and/or postemergence weed control in crops such as wheat corn, soybeans, rice, and cotton. While none of the compounds are selective for use in all crops, by all methods of application, and at all rates of application, each is active as a herbicide and most are selective for use in one or more crops at some application rates and by some methods of application. The data provided herein in the examples can be used as a guide in choosing appropriately selective compounds from the compounds of Formulae I and II, appropriate application methods, and appropriate application rates for controlling unwanted vegetation in various crops. It is well within the skill of those in the art to select appropriate compounds of Formula I and II not mentioned in the examples using the information herein and routine procedures.

Certain of the compounds of Formula I, notably those wherein X and Z represent C_1–C_4 alkyl, are resistant to degradation in the environment and, therefore, have limited utility as selective herbicides in crops where crop rotation programs are practiced except where the soil and climate are especially favorable for degradation. These compounds, on the other hand, are particularly useful as industrial herbicides where multi-year control is desired.

For all such uses, unmodified active ingredients of the present invention can be employed. However, the present invention embraces the use of a herbicidally-effective amount of the active ingredients in composition form with an inert material known in the art as an agricultural adjuvant or carrier in solid or liquid form. Such adjuvants or carriers must not be phytotoxic to valuable crops particularly at the concentration employed in applying the composition in attempting selective weed control in the presence of crops. If weed control is desired in the absence of crops, it is generally sufficient to employ adjuvants or carriers which do not leave a persistent phytotoxic residue.

Thus, for example, an active ingredient can be dispersed on a finely-divided solid and employed therein as a dust. Also, the active ingredients, as liquid concentrates or solid compositions comprising one or more of the active ingredients can be dispersed in water, typically with aid of a wetting agent, and the resulting aqueous dispersion employed as a spray. In other procedures the active ingredients can be employed as a constituent of organic liquid compositions, oil-in-water and water-in-oil emulsions or dispersions, with or without the addition of wetting, dispersing, or emulsifying agents.

Suitable adjuvants of the foregoing type are well known to those skilled in the art. The methods of applying the solid or liquid herbicidal formulations similarly are well known to the skilled artisan.

Organic solvents that can be employed include toluene, xylene, kerosene, diesel fuel, fuel oil, and petroleum naphtha, ketones such as acetone, methylethyl ketone and cyclohexanone, chlorinated hydrocarbons such as trichloroethylene, and perchloroethylene, esters such as ethyl acetate, amyl acetate and butyl acetate, ethers, e.g., ethylene glycol monomethyl ether and diethylene glycol monomethyl ether, alcohols, e.g., methanol, ethanol, isopropanol, amyl alcohol, ethylene glycol, propylene glycol, butylcarbitol acetate and glycerine. Mixtures of water and organic solvents, either as emulsions or solutions, can be employed.

The active ingredients of the present invention can also be applied as aerosols, e.g., by dispersing them by means of a compressed gas such as one of the fluorocarbons or one of its hydrocarbon successors.

The active ingredients of the present invention can also be applied with solid adjuvants or carriers such as talc, pyrophyllite, synthetic fine silica, attapulgus clay, kieselguhr, chalk, diatomaceous earth, lime, calcium carbonate, bentonite, Fuller's earth, cotton seed hulls, wheat flour, soybean flour, pumice, tripoli, wood flour, walnut shell flour, redwood flour and lignin.

As stated, it is frequently desirable to incorporate a surface-active agent in the compositions of the present invention. Such surface-active or wetting agents are advantageously employed in both the solid and liquid compositions. The surface-active agent can be anionic, cationic or nonionic in character.

Typical classes of surface-active agents include alkyl sulfonate salts, alkylaryl sulfonate salts, alkylaryl polyether alcohols, fatty acid esters of polyhydric alcohols and the alkylene oxide addition products of such esters, and addition products of long-chain mercaptans and alkylene oxides. Typical examples of such surface-active agents include the sodium alkylbenzene sulfonates having 10 to 18 carbon atoms in the alkyl group, alkyl phenol ethylene oxide condensation products, e.g., p-isooctylphenol condensed with 20 ethylene oxide units, soaps, e.g., sodium stearate and potassium oleate, sodium salt of propylnaphthalene sulfuric acid, di(2-ethylhexyl)ester of sodium sulfosuccinic acid, sodium lauryl sulfate, sodium decyl sulfonate, sodium salt of the sulfonated monoglyceride of coconut fatty acids, sorbitan sesquioleate, lauryl trimethyl ammonium chloride, octadecyl trimethyl ammonium chloride, polyethylene glycol lauryl ether, polyethylene glycol esters of fatty acids and rosin acids, e.g., Ethofat® 7 and 13, sodium N-methyl-N-oleyl taurate, sodium dibutylnaphthalene sulfonate, sodium lignin sulfonate, polyethylene glycol stearate, sodium dodecyl benzene sulfonate, tertiary dodecyl polyethylene glycol thioether (nonionic 218), long-chain ethylene oxide-propylene oxide condensation products e.g., Pluronic® 61 (molecular weight about 1000), polyethylene glycol ester of tall oil acids, sodium octophenoxyethoxyethyl sulfate, tris(polyoxyethylene)sorbitan monostearate (Tween® 60), and sodium dihexylsulfosuccinate.

The herbicidally effective concentration of the active ingredients in solid or liquid compositions generally is from about 0.00003 to about 95 percent by weight or more. Concentrations from about 0.05 to about 50 percent by weight are often employed. In compositions to be employed as concentrates, the active ingredient can be present in a concentration from about 5 to about 98 weight percent, preferably 15–50 weight percent. The active ingredient compositions can also contain other compatible additaments, for example, phytotoxicants, plant growth regulants, pesticides and the like and can be formulated with solid particulate fertilizer carriers such as ammonium nitrate, urea and the like.

In further embodiments, the compounds of the present invention or compositions containing the same, can be advantageously employed in combination with one or more additional pesticidal compounds. Such additional pesticidal compounds may be insecticides, nematocides, miticides, arthropodicides, herbicides, fungicides or bactericides that are compatible with the compounds of the present invention in the medium selected for application. In such embodiments, the pesticidal compound is employed as a supplemental toxicant for the same or for a different pesticidal use or as an additament.

The compounds of the present invention are particularly useful in combination with other herbicides including, for example, the substituted urea herbicides such as 3-(3,4-dichlorophenyl)-1,1-dimethylurea, 3-(3,4-dichlorophenyl)-1-methoxy-1-methylurea (Lorox®) and 1,1-dimethyl-3-(α,α,α-trifluoro-m-tolyl)urea (Cotoran®); the triazines such as 2-chloro-4-(ethylamino)-6-(isopropylamino)-s-triazine and 2-chloro-4-(1-cyano-1-methylethylamino)-6-ethylamino-s-triazine (Bladex®); the uracils such as 5-bromo-3-sec-butyl-6-methyluracil; N-(phosphonomethyl)glycine; the phenoxies such as 2,4-dichlorophenoxyacetic acid; picolinic acids such as 4-amino-3,5,6-trichloropicolinic acid (Tordon®) and 3,6-dichloropicolinic acid (Lontrel®); 4-chloro-2-butynyl-3-chlorophenyl carbamate (Carbyne®); diisopropylthiocarbamic acid; ester with 2,3-dichloroallyl alcohol (Avadex®); diisopropylthiocarbamic acid, ester with 2,3,3-trichloroallyl alcohol (Avadex® BVD); ethyl-N-benzoyl-N-(3,4-dichlorophenyl)-2-aminopropionate (Suffix®); 1,2-dimethyl-3,5-diphenylpyrazolium methylsulfate (Avenge®); methyl (2-[4-

(2,4-dichlorophenoxy)phenoxy]propanoate) (Hoelon®); butyl 2-[4-[(5-(trifluoromethyl)-2-pyridinyl-)oxy]phenoxy]propanoate (Fusilade®); esters of 2-[4-[(3-chloro-5-trifluoromethyl)-2-pyridinyl)oxy]phenoxy]propionic acid; 4-amino-6-tert-butyl-3-(methylthio)-1,2,4-triazin-5-(4H)-one (Lexone®); 3-isopropyl-1H-2,1,3-benzothiadiazin-(4)-3H-one 2,2-dioxide; α,α,α-trifluoro-2,6-dinitro-N,N-dipropyl-p-toluidine; 1,1'-dimethyl-4,4'-bipyridinium ion; 2-chloro-2',6'-diethyl(-methoxymethyl)acetanilide; and 2-[1-(ethoxyimino)-butyl]-5-[(2-ethylthio)propyl]-3-hydroxy-2-cyclohexen-1-one (Poast®).

The rates of application for compounds of the invention are determined by a number of factors including the active ingredient being applied, the particular action desired (e.g., general or selective control), the plant species to be modified and the stage of growth thereof, the part of the plant to be contacted with the toxic active ingredient, the formulation selected, weather and climate, etc. Thus, it is to be understood that all of the active ingredients of the present invention and compositions containing the same may not be equally effective at similar concentrations or against the same plant species. In non-selective preemergence and foliar treatments, the active ingredients of the invention are usually applied at an approximate rate of from about 0.01 to about 10 pounds/acre. In pre- and postemergence operations for selective uses, a dosage of about 0.01 to about 10 pounds/acre is generally applicable, a rate of 0.01 to 4 pounds/acre being preferred.

The following example illustrates the effect of the compounds of this invention applied postemergently.

Plant species in this and other tests were the following:

	Common Name	Scientific Name
A.	cotton	Gossypium spp.
B.	rape	*Brassica napus*
C.	soybean	*Glycine max.*
D.	sugar beet	*Beta saccharifera*
E.	cocklebur	Xanthium spp.
F.	jimsonweed	*Datura stramonium*
G.	annual morning glory	Ipomoea spp.
H.	pigweed	Amaranthus spp.
I.	velvetleaf	*Abutilon theophrasti*
J.	corn	*Zea mays*
K.	rice	*Oryza sativa*
L.	sorghum	*Sorghum vulgare*
M.	wheat	*Triticum aestivum*
N.	barnyardgrass (watergrass)	*Echinochloa crusgalli*
O.	crabgrass	Digitaria spp.
P.	yellow foxtail	*Setaria lutescens*
Q.	johnson grass	*Sorghum halepense*
R.	wild oats	*Avena fatua*
S.	sprangletop	*Leptochloa filiformis*
T.	yellow nutsedge	*Cyperus esculentus*

EXAMPLE 118

In representative operations, each compound to be utilized in a series of tests is dissolved in acetone to one-half of the final volume (twice the final concentration) to be used and the acetone solution in each case is admixed with an equal volume of water containing 0.1 percent by weight of surface active material. The compositions, generally in the nature of an emulsion, were employed to spray separate respective plant species which had been grown to a 2–4 leaf stage in soil or good nutrient content in a greenhouse. Sufficient amounts were employed to provide various application rates as listed in the table. The various beds were positioned side by side and exposed to substantially identical conditions of temperature and light. Each bed was maintained so as to prevent any interaction with test compounds in different seed beds. Other plants were left untreated to serve as controls. After treatment, the plants were maintained for about two weeks under greenhouse conditions conducive for good plant growth and watered as necessary. The specific plant species test compound and dosage and the percent post-emergent control obtained at one or more dosages tested are set forth in the table below. Control refers to the reduction in growth compared to the observed result of the same untreated species.

POSTEMERGENT CONTROL OF PLANT SPECIES

Compound	Dosage (ppm)	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	T
1	15.6	90	100	95	—	95	60	85	98	100	100	98	100	100	95	—	95	98	90	70
2	1000	10	50	40	90	80	90	10	0	50	0	20	0	0	0	0	0	90	0	0
4	500	10	40	40	70	40	60	0	0	60	0	40	40	0	0	20	0	80	0	0
6	500	60	80	70	90	90	30	80	30	90	0	20	80	0	35	20	0	80	0	90
7	500	—	90	55	100	100	20	90	60	65	0	15	65	0	35	0	25	50	0	65
8	500	—	90	75	95	90	90	70	50	75	20	40	70	10	70	10	25	90	0	60
	62.5	—	60	40	60	70	15	35	40	20	0	30	20	0	5	0	10	20	0	0
9	1000	50	60	65	80	90	90	20	80	40	0	30	90	0	20	40	0	30	0	40
10	2000	15	30	50	75	90	0	0	100	15	10	—	10	0	0	0	0	0	0	60
	500	0	10	20	60	15	0	0	20	0	0	—	0	0	0	0	0	0	0	0
12	500	—	100	80	95	100	70	100	100	95	10	25	75	0	80	25	20	55	0	90
	125	—	95	80	95	100	20	60	90	75	0	10	60	0	10	0	0	25	0	40
	15.6	—	75	60	65	90	0	20	70	0	0	0	0	0	0	0	0	0	0	0
13	250	95	100	95	100	100	90	90	100	95	15	15	90	0	90	20	70	90	0	90
	62.5	95	100	95	95	100	50	90	100	80	0	0	80	0	100	0	50	85	0	75
	15.6	60	90	85	90	100	30	85	70	70	0	0	80	0	0	0	0	70	0	0
14	1000	20	—	25	90	80	0	10	60	0	0	30	0	0	0	0	0	0	0	0
15	1000	—	70	25	40	80	0	70	40	60	0	35	40	0	0	0	0	0	0	10
17	1000	20	95	15	15	10	0	0	60	85	30	0	60	10	0	15	10	85	0	0
	500	15	70	15	10	10	0	0	50	70	20	0	40	0	0	0	20	60	0	0
19	1000	90	90	90	100	90	95	40	100	80	0	0	50	0	20	20	0	65	0	85
21	1000	90	100	70	95	95	0	45	80	30	0	20	30	0	0	0	0	20	0	80
22	250	100	100	95	100	100	100	100	100	95	25	50	90	10	100	90	100	100	20	85
	62.5	95	100	90	100	100	95	80	100	95	15	20	90	0	100	75	90	100	0	80
	15.6	85	95	90	90	90	80	75	95	90	0	0	75	0	100	0	95	85	0	40
24	1500	40	90	40	70	90	—	0	—	50	0	20	10	0	0	—	—	10	0	0
25	250	100	100	90	100	100	100	80	100	95	70	60	85	0	90	90	95	100	20	80
	62.5	90	100	80	100	100	100	35	100	60	40	10	80	0	70	70	90	90	0	60
	15.6	30	—	70	90	90	80	20	100	40	20	0	60	0	20	0	70	75	0	0
26	500	100	100	95	100	100	100	90	100	100	80	80	90	30	100	90	90	100	0	90
	125	100	100	85	100	100	100	85	100	90	80	40	85	0	100	80	75	95	0	80
	31.25	90	100	80	95	90	60	75	100	40	20	0	50	0	100	20	30	60	0	80
30	500	0	40	30	0	40	0	60	0	40	0	20	0	0	0	0	0	0	0	0
31	125	90	100	95	100	90	100	60	85	90	40	0	90	0	40	80	90	100	0	75
	31.25	75	95	90	90	75	80	40	80	95	50	0	80	0	20	75	80	100	0	80
	7.8	60	60	75	100	60	60	0	55	85	30	0	50	0	0	0	60	80	0	50
32	500	20	0	15	30	15	60	0	0	50	0	10	0	30	0	10	10	95	0	0
	250	30	0	15	0	0	30	0	0	40	0	20	0	0	0	0	0	80	0	0
33	500	50	60	40	40	60	40	60	10	80	25	0	80	0	0	0	0	60	0	10
34	500	70	100	90	100	100	90	75	100	100	0	0	60	0	0	0	0	20	0	60
35	500	0	70	70	80	95	30	40	90	0	0	0	20	—	0	0	0	0	0	0
38	62.5	80	98	90	100	98	60	80	98	98	0	0	20	0	10	10	95	90	0	30
	15.6	10	98	70	98	95	50	50	80	40	0	0	0	0	0	5	80	50	0	10
39	62.5	98	98	98	98	100	90	98	100	98	0	0	65	0	50	70	97	90	0	40
	15.6	80	98	98	98	95	90	95	95	98	0	0	80	0	40	0	90	80	0	20
	3.9	40	95	40	98	90	40	70	70	40	0	0	5	0	0	0	80	0	0	0
40	1000	25	90	25	90	80	60	20	75	20	0	0	20	0	0	0	0	0	0	20
41	4000	30	—	—	—	—	—	70	—	98	—	—	—	—	80	40	40	—	—	95
43	2000	0	20	15	0	0	0	0	—	0	0	0	0	0	0	25	0	20	0	0

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POSTEMERGENT CONTROL OF PLANT SPECIES

Compound	Dosage (ppm)	Plant Species A.	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	T
44	250	40	80	75	80	85	20	75	90	80	0	0	20	0	0	0	40	0	0	60
45	500	0	70	60	70	25	0	10	—	50	0	50	0	0	0	0	0	0	0	0
46	31.3	95	98	98	98	98	95	98	100	98	15	0	0	0	0	10	80	50	0	40
	7.8	80	95	98	98	98	80	98	100	98	15	0	0	0	0	0	0	0	0	20
	1.9	60	98	95	95	95	30	90	90	95	15	0	0	0	0	0	0	0	0	10
47	62.5	70	90	98	100	98	20	98	90	98	0	0	0	0	0	0	0	0	0	10
48	500	10	75	55	70	70	30	60	—	40	0	0	0	0	0	0	0	0	0	0
49	250	90	100	95	100	100	100	95	90	100	0	10	80	0	90	80	95	80	20	90
	62.5	95	100	95	100	100	100	95	80	100	0	0	70	0	80	60	90	100	0	90
50	62.5	98	100	100	100	98	98	98	98	100	93	97	90	0	95	95	99	97	90	90
	15.6	90	100	98	90	98	90	80	90	100	70	97	50	0	80	80	97	95	10	80
51	62.5	98	98	98	98	100	95	98	90	100	40	40	90	0	20	0	93	95	10	80
	7.8	30	70	80	95	95	60	90	20	70	0	0	50	0	0	0	0	20	0	70
52	2000	70	10	70	50	70	0	—	0	0	0	0	0	0	0	0	0	0	0	0
53	62.5	90	100	98	100	100	98	90	100	100	0	10	90	0	70	50	95	97	0	60
	15.6	60	98	98	98	98	98	90	100	98	0	0	90	0	65	20	97	93	0	80
54	62.5	98	98	98	100	98	90	98	98	98	30	40	93	20	50	30	95	97	15	30
	7.8	60	98	80	98	98	40	40	90	50	0	0	25	0	0	0	25	60	0	0
55	125	25	70	15	95	80	25	20	20	20	0	0	0	0	0	0	0	0	0	0
56	62.5	85	95	90	100	99	85	80	95	90	0	0	55	0	0	40	75	95	0	15
57	125	20	95	10	85	80	0	0	0	—	0	0	70	—	0	0	0	85	0	0
58	125	90	100	95	100	100	95	95	100	100	85	60	95	60	95	90	90	100	—	90
	31.25	90	100	95	100	100	95	90	100	95	75	50	90	0	90	95	90	95	—	90
59	250	0	70	10	40	75	50	0	0	—	0	0	0	0	0	0	0	0	0	0
60	2000	60	—	15	—	—	50	80	100	80	—	0	10	0	—	0	0	—	—	15
61	125	40	75	90	90	30	75	5	60	40	0	15	0	0	0	70	25	35	0	5
62	125	40	80	90	70	80	75	65	75	80	0	15	45	0	0	10	10	80	0	15
63	62.5	90	90	90	90	95	95	80	90	90	0	10	60	0	50	40	65	60	0	60
64	125	100	99	90	100	—	95	80	100	100	85	70	80	80	0	90	80	90	0	80
65	250	—	85	75	60	—	10	0	40	—	70	0	70	0	50	70	90	90	0	15
66	1000	50	80	0	90	—	0	0	95	30	0	0	20	0	0	30	0	80	0	0
67	1000	40	70	0	30	—	0	0	100	30	0	0	0	0	0	20	20	0	0	0
68	1000	70	80	60	100	100	75	50	100	90	0	25	80	0	30	80	95	75	0	75
	125	80	50	40	40	60	25	0	65	50	0	0	25	0	0	0	50	60	0	20
69	500	90	90	40	100	—	90	80	100	85	90	0	80	0	80	80	90	95	0	80
	62.5	75	80	5	40	—	50	60	100	50	40	0	40	0	0	0	70	30	0	60
70	250	90	95	70	90	95	95	80	50	85	0	0	0	0	0	75	80	80	0	90
71	500	75	70	35	70	0	60	0	0	70	0	0	0	0	0	20	0	0	0	0
72	62.5	100	100	85	50	100	90	85	70	100	0	35	50	0	50	0	40	70	0	85
73	125	0	50	50	30	80	70	20	40	50	0	0	0	0	0	0	0	0	0	25
74	500	70	100	80	100	100	90	80	70	100	0	0	80	0	70	0	60	50	0	95
75	125	25	65	40	0	75	40	0	0	100	0	20	0	0	10	0	0	0	0	5
76	125	80	95	90	90	90	100	90	100	100	40	80	40	20	35	65	98	60	10	95
	31.25	60	95	80	60	70	50	80	80	98	30	70	50	0	30	50	85	30	0	80
77	125	80	100	90	80	85	100	95	100	100	10	30	0	0	40	20	98	20	0	15
	15.6	50	—	75	20	50	80	50	20	80	0	15	0	0	0	0	40	20	0	15
78	125	75	95	90	85	40	0	0	100	90	0	50	50	0	10	10	50	0	0	75
79	2000	80	90	70	90	75	85	15	30	75	0	0	75	0	10	0	0	60	25	0
81	2000	50	—	10	0	—	20	0	30	40	0	0	0	0	0	0	0	0	0	40

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POSTEMERGENT CONTROL OF PLANT SPECIES

Compound	Dosage (ppm)	Plant Species A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	T
82	500	85	100	85	95	85	90	85	100	85	0	0	0	0	0	0	0	0	0	0
83	62.5	50	60	10	60	20	0	0	0	30	0	0	0	0	0	0	0	0	0	0
84	2000	30	100	40	100	—	—	0	100	98	0	0	0	0	0	0	0	0	0	30
85	62.5	70	—	80	100	70	70	75	100	80	30	0	40	0	50	50	75	0	0	60
	7.8	50	—	80	100	55	80	55	100	80	0	0	20	0	0	0	70	0	0	50
86	125	50	80	80	100	60	—	0	100	65	0	0	40	0	30	0	70	0	0	20
87	250	50	80	75	100	40	50	40	70	60	0	0	20	0	0	0	0	0	20	30
89	2000	50	—	35	80	70	85	20	100	90	0	10	30	0	0	50	40	0	0	50
90	500	0	70	50	—	75	70	30	100	50	0	0	0	0	0	—	70	20	0	0
91	62.5	100	100	90	100	100	100	90	100	100	0	0	0	0	0	0	95	20	0	95
92	62.5	25	50	80	0	—	90	80	60	50	40	0	0	0	0	0	0	0	0	0
93	500	0	70	90	70	80	80	0	70	20	0	0	0	0	0	0	0	0	0	15
94	2000	0	60	85	100	80	70	0	70	70	0	0	25	0	20	0	0	0	0	80
97	1000	70	90	70	90	90	20	50	100	80	0	30	55	0	60	0	70	60	0	0
98	4000	60	—	—	—	—	60	100	90	—	—	—	—	—	0	30	98	—	0	0
99	2000	25	80	60	65	0	0	0	50	20	0	20	0	0	0	0	0	0	0	0
101	2000	40	—	50	100	50	80	0	100	35	0	30	0	0	20	0	80	0	0	50
103	4000	0	—	—	—	—	—	100	100	80	—	—	—	—	0	0	0	—	0	—
104	125	65	95	90	100	85	100	100	100	100	100	100	100	80	100	100	100	100	80	80
	3.9	35	85	80	100	70	75	90	100	90	85	85	95	50	100	—	100	95	50	60
105	500	35	40	95	90	100	60	70	60	0	80	20	0	0	20	0	—	0	0	0
106	500	30	40	90	0	90	0	80	40	0	90	30	40	20	30	0	0	90	30	0
	250	0	20	90	0	40	0	80	20	0	50	10	30	0	0	0	0	80	20	0
107	1000	0	50	85	15	80	0	0	40	25	0	0	40	0	0	0	0	75	0	0
108	500	70	40	75	70	80	30	10	0	90	80	0	80	60	100	0	0	100	0	35
	125	60	25	75	35	70	15	0	0	20	85	0	90	0	100	0	0	80	0	5
111	250	25	90	70	90	95	50	80	70	85	0	0	10	0	0	0	0	50	0	60
112	125	0	90	85	90	95	65	80	60	85	0	0	60	0	0	0	0	15	0	40
113	250	30	70	15	90	90	50	80	70	75	0	0	50	0	0	0	0	10	0	60
114	1000	25	95	40	100	100	100	80	—	90	0	0	25	85	90	0	40	30	0	75
	62.5	0	50	25	0	20	60	0	0	60	0	0	0	0	0	0	0	0	0	0
116	250	100	—	45	100	95	90	25	95	90	0	0	0	0	10	0	65	0	0	50
117	500	90	100	35	100	100	100	80	75	100	0	0	60	0	0	0	65	75	0	25
	62.5	60	75	0	80	90	90	50	40	50	0	0	15	0	0	0	40	25	0	0
118	500	0	80	0	100	100	100	70	70	80	0	0	0	—	0	60	20	0	0	70
119	500	0	100	0	50	70	90	30	0	70	30	0	0	0	0	0	0	80	0	40
120	250	100	90	98	80	98	90	100	100	80	0	98	35	0	0	0	70	0	0	70
133	4000	20	—	—	—	—	—	40	100	40	—	—	—	—	0	0	0	—	0	0
135	2000	0	50	40	90	75	75	0	—	75	0	0	10	0	0	0	0	0	0	0
136	500	30	80	30	80	98	30	40	90	70	0	0	0	0	0	0	0	0	0	0
137	1000	—	—	50	100	70	100	100	100	80	0	50	50	25	75	98	80	80	50	50
	62.5	40	—	35	90	30	70	50	100	75	0	30	0	0	60	20	75	20	0	20
138	125	70	100	40	80	80	80	50	100	85	0	80	50	30	80	60	85	70	0	0
	31.2	40	98	0	70	70	50	0	100	65	0	0	0	0	20	0	85	70	0	0
139	125	60	98	50	100	100	85	90	100	100	0	0	65	20	0	20	75	80	0	40
140	125	90	100	65	100	100	95	100	100	90	0	100	95	30	80	80	80	100	50	35
	31.2	95	100	50	100	100	80	50	100	85	0	55	70	0	20	50	98	90	0	0
141	125	60	98	80	100	70	98	90	100	98	0	80	65	50	80	95	100	80	70	80
	31.2	60	100	75	100	65	80	80	100	95	0	80	55	0	75	0	80	80	0	60

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POSTEMERGENT CONTROL OF PLANT SPECIES

Compound	Dosage (ppm)	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	T
142	2000	80	75	50	95	100	80	75	—	35	0	0	75	0	0	50	80	80	0	0
143	62.5	98	100	60	100	95	50	100	100	0	70	93	0	93	60	97	97	97	0	90
	15.6	98	98	20	100	90	20	100	100	0	50	30	0	35	50	80	80	80	0	70
	3.9	80	70	0	98	40	0	60	90	0	0	0	0	0	10	70	70	0	0	0
144	62.5	80	95	15	100	99	99	80	100	100	0	75	80	0	80	100	95	100	0	85
	7.8	55	70	0	100	85	70	35	95	95	0	15	25	0	50	40	90	10	0	55
145	62.5	75	90	35	100	100	90	95	100	100	0	—	80	0	15	25	75	75	0	20
	7.8	50	65	0	95	95	55	65	100	75	0	—	45	0	0	0	0	65	0	0
146	62.5	50	95	85	100	100	95	95	100	100	15	90	75	0	95	95	95	90	—	85
	3.9	20	50	5	70	90	75	60	75	75	0	40	10	0	20	0	75	25	—	55
147	15.6	80	90	45	100	—	90	80	100	100	0	0	0	0	0	20	80	40	0	80
	3.9	25	70	5	100	—	60	60	90	90	0	0	0	0	0	0	0	0	0	15
148	25	75	—	0	—	—	80	0	100	90	—	—	70	0	—	60	95	—	—	90
149	2000	0	—	0	—	—	0	0	100	10	—	—	0	0	—	0	90	—	—	0
150	125	10	70	0	90	90	90	35	70	80	0	0	0	0	10	0	80	25	0	65
151	62.5	95	100	25	—	100	100	95	100	95	0	25	40	0	80	0	85	—	0	95
	15.6	80	75	0	—	100	100	90	100	95	0	0	0	0	30	0	85	—	0	90
152	125	100	100	45	100	100	100	100	100	100	0	50	80	0	100	0	100	90	0	95
	7.8	90	90	0	90	80	80	85	90	100	0	0	40	0	55	0	90	65	0	90
153	125	90	100	35	100	100	100	85	100	100	0	50	80	0	90	25	100	80	0	90
	7.8	70	100	0	100	60	70	55	40	90	0	0	20	0	70	0	55	0	0	80
154	62.5	40	90	0	80	95	90	50	20	90	0	25	0	0	0	0	0	0	0	30
155	125	90	100	20	100	100	95	85	100	100	0	20	75	10	15	0	75	75	0	95
	15.6	75	90	0	95	50	80	15	80	95	0	0	15	0	0	0	50	10	0	80
156	31.25	75	90	0	100	90	100	85	100	100	0	40	20	0	0	0	0	10	0	85
157	15.6	70	90	0	80	50	90	40	70	90	0	0	80	0	0	0	75	80	0	0
158	31.25	75	95	20	100	40	90	60	90	95	0	0	50	0	10	0	70	50	0	0
	7.8	45	80	10	90	0	80	10	40	65	0	0	0	0	0	0	25	0	0	0
159	125	100	100	25	100	100	100	100	100	100	0	35	75	—	100	0	75	100	0	90
	15.6	50	100	0	100	70	100	70	70	95	0	15	50	—	50	0	60	40	0	10
160	62.5	65	80	65	100	75	—	60	100	100	0	0	50	0	30	50	70	30	0	100
161	250	80	85	40	80	65	100	75	100	60	15	0	65	0	15	30	50	10	0	50
162	62.5	40	80	0	—	10	70	20	95	80	0	40	55	0	15	30	70	0	0	0
163	500	0	70	0	0	40	70	0	90	20	0	0	0	0	0	0	50	0	0	0
164	125	90	95	30	100	80	95	80	100	100	0	0	85	0	65	0	70	75	0	70
	31.25	60	90	0	100	50	50	10	100	90	0	0	15	0	0	0	60	0	0	85
165	62.5	70	70	30	90	50	50	60	100	80	0	0	0	0	50	0	70	20	0	80
	15.6	45	40	0	70	20	50	40	80	45	0	0	0	0	20	0	50	25	0	60
166	62.5	60	65	55	70	70	60	75	100	90	80	0	0	0	80	80	85	100	30	70
	15.6	40	40	40	60	20	50	50	100	80	0	0	0	0	65	0	50	0	0	60
168	62.5	60	—	80	—	70	70	98	100	90	0	0	0	0	0	90	80	—	0	80
	15.6	20	90	80	—	50	—	75	100	60	0	0	0	0	0	0	75	—	0	—
169	125	50	80	0	80	30	70	0	70	65	0	0	20	0	0	0	0	0	0	0
170	500	50	—	30	95	25	90	70	100	90	25	35	25	0	75	60	80	85	80	98
	125	50	100	0	90	15	80	60	100	80	0	30	50	0	40	60	70	80	40	—
171	2000	60	30	—	90	0	50	0	0	50	0	—	0	0	0	—	0	0	0	0
172	1000	40	80	50	80	20	70	20	100	70	0	0	0	0	0	0	40	0	0	50
173	125	0	80	40	100	0	—	0	80	0	0	25	0	—	0	—	20	50	0	0
174	62.5	80	—	70	90	80	85	100	100	100	20	70	70	25	80	98	80	85	85	90

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POSTEMERGENT CONTROL OF PLANT SPECIES

Compound	Dosage (ppm)	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	T
		Plant Species																		
	7.8	100	80	50	90	40	80	70	100	90	0	30	20	0	40	20	80	40	40	100
175	62.5	100	—	40	100	100	100	100	100	100	0	30	80	0	100	100	100	80	40	20
176	250	0	95	65	80	0	80	50	100	80	0	0	20	0	0	0	20	100	0	0
177	62.5	90	98	80	90	98	85	80	100	100	50	98	90	50	100	80	98	98	60	65
	7.8	50	85	60	80	50	40	80	100	100	0	80	50	0	80	50	95	80	20	45
178	250	50	90	50	80	90	85	35	—	80	0	75	0	0	0	0	0	0	0	0
179	62.5	0	50	10	75	50	15	0	0	0	0	0	0	0	0	0	0	0	0	0
180	500	100	100	100	100	100	100	90	—	100	0	10	50	0	10	90	75	20	0	90
	125	95	100	90	100	100	100	90	—	100	0	0	40	0	0	40	60	0	0	40
181	125	90	99	95	90	80	—	80	100	95	0	0	50	0	0	0	95	40	0	0
182	125	90	98	95	—	100	98	60	100	98	0	0	0	0	0	20	95	20	30	20
183	125	65	95	0	98	50	90	0	95	90	0	0	20	0	0	20	20	20	0	0
184	125	95	100	90	—	90	100	85	100	100	0	0	50	0	0	20	80	30	100	50
185	62.5	90	98	—	95	90	90	50	—	90	0	—	50	0	0	—	—	20	0	0
186	4000	100	—	—	—	—	—	80	100	100	—	—	—	—	50	70	90	—	30	90
187	125	40	—	90	85	80	80	80	98	90	0	0	0	0	0	0	70	0	0	70
188	125	90	80	95	85	60	80	100	100	90	0	50	50	20	70	80	80	60	70	70
189	125	80	100	85	100	25	80	80	90	90	0	25	50	0	70	50	70	40	25	70
190	125	98	80	85	100	80	—	20	100	85	15	0	40	0	0	20	85	40	0	0
191	125	60	100	80	95	70	100	80	98	98	0	80	70	30	100	60	100	90	65	30
	31.2	40	100	80	80	20	80	80	50	70	0	50	70	0	75	20	100	80	50	30
192	125	80	100	20	100	—	90	90	100	90	0	0	0	0	0	0	40	0	0	98
	31.25	40	90	0	100	—	80	40	100	20	0	0	0	0	0	0	0	0	0	90
193	250	80	100	40	100	30	100	80	100	98	0	20	0	0	60	60	90	75	0	65
194	250	50	100	60	100	70	100	10	100	95	0	0	10	0	0	30	80	25	0	70
195	250	80	90	65	100	25	85	80	98	100	0	0	0	0	20	20	80	30	0	60
196	250	70	100	40	100	90	100	100	100	100	0	0	30	10	20	70	80	40	10	70
197	250	80	85	40	80	65	100	75	100	60	15	0	65	0	15	30	50	10	0	50
198	2000	60	100	0	90	0	0	50	30	90	0	0	0	0	0	0	0	0	0	0
199	62.5	40	100	90	90	—	40	10	98	80	0	0	0	0	0	0	0	0	0	0
200	62.5	0	95	35	95	—	30	0	40	50	0	0	0	0	0	0	0	0	0	35
201	500	0	20	0	50	80	70	0	90	60	0	0	0	0	0	0	0	0	0	0
204	1000	70	60	15	60	—	50	0	0	90	0	0	10	0	0	0	0	0	0	10
205	250	—	75	60	95	—	60	40	100	—	45	0	80	0	40	95	95	100	0	60
206	250	40	100	20	100	100	90	98	100	98	0	0	0	0	0	20	90	80	0	80
207	1000	90	100	25	100	95	95	50	30	100	0	0	0	0	20	0	20	40	0	70
208	62.5	80	100	65	95	65	95	50	100	90	0	0	15	0	0	0	50	0	0	25
209	250	0	70	0	40	80	70	0	0	70	0	0	0	0	0	0	0	0	0	0
210	62.5	35	30	20	40	0	—	0	0	55	0	0	0	0	0	0	0	0	0	0
211	1000	20	—	0	40	20	—	0	75	60	0	0	10	0	0	0	0	25	0	0
212	2000	0	—	55	98	50	—	0	100	70	0	0	50	0	0	0	0	0	—	0
213	125	95	100	90	100	70	100	80	100	100	98	20	85	0	70	90	100	100	50	65
	31.2	90	30	80	100	50	80	70	100	98	98	0	85	0	35	90	100	98	30	50
214	62.5	75	—	90	100	70	—	50	100	—	90	35	100	70	80	20	100	98	50	80
215	62.5	80	—	90	80	70	80	50	100	98	90	30	85	20	90	80	85	100	40	65
216	62.5	80	—	85	100	70	80	95	100	80	90	0	50	40	80	80	80	80	50	70
217	31.2	0	—	75	—	40	60	70	100	85	80	30	70	0	80	100	60	75	0	35
218	62.5	20	—	90	—	40	80	80	100	85	0	0	30	0	0	80	25	0	0	0
219	62.5	80	—	90	98	60	—	80	100	90	90	0	60	25	60	70	85	85	0	—

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POSTEMERGENT CONTROL OF PLANT SPECIES

Compound	Dosage (ppm)	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	T
		Plant Species																		
	15.6	65	—	80	90	35	—	40	100	90	0	0	50	0	0	50	70	70	0	0
220	62.5	—	50	80	—	45	50	50	100	85	90	55	60	0	80	90	85	60	70	0
221	62.5	—	—	50	—	60	80	80	100	—	75	0	—	0	50	80	75	90	0	70
222	62.5	—	—	80	—	30	100	80	100	—	75	0	—	0	0	0	50	50	0	70
223	125	65	98	80	100	60	100	100	100	100	100	70	100	100	100	100	100	100	80	70
	15.6	50	90	80	80	40	100	90	100	90	98	80	100	80	98	45	100	100	70	55
227	250	0	—	0	—	80	70	80	100	50	40	30	25	0	0	0	80	50	40	50
	31.2	0	—	0	20	50	50	50	100	0	0	0	20	0	0	0	40	30	0	0
228	125	0	50	0	80	90	50	0	100	40	20	0	0	0	0	80	0	60	0	0
229	125	30	100	80	100	100	60	70	100	98	0	—	0	—	0	20	70	50	0	20
	31.2	0	98	70	75	98	40	50	100	75	0	50	0	0	0	0	50	0	0	20
230	125	0	70	50	80	70	80	35	100	85	80	0	55	0	0	0	55	70	0	50
231	125	25	98	65	100	80	100	100	100	85	100	90	100	90	100	100	100	100	60	75
	31.2	0	90	50	100	70	80	80	100	50	95	80	75	70	80	50	100	95	40	70
232	4000	50	—	—	—	—	—	10	0	50	—	—	—	—	0	0	0	—	0	80
233	250	0	80	40	0	20	30	—	50	50	0	20	0	0	0	0	0	0	0	0
234	4000	60	—	—	—	—	—	0	100	0	—	—	—	—	0	0	0	—	—	20
235	1000	20	70	30	50	70	70	20	100	—	90	20	35	25	75	98	45	75	60	0
236	1000	0	—	60	80	75	80	70	100	70	0	20	0	0	50	70	80	25	50	70
237	1000	50	70	80	30	70	—	50	100	80	75	50	45	40	40	0	80	85	65	0
239	4000	90	—	—	—	—	—	98	100	90	—	—	—	—	20	20	50	—	30	90
240	2000	—	—	50	100	20	60	30	100	80	20	0	20	0	25	70	80	50	0	65
241	2000	0	—	30	50	0	0	20	98	30	0	0	0	0	0	75	75	0	0	70
242	2000	0	—	0	70	40	0	0	0	70	0	20	0	0	0	15	0	0	—	0
243	500	80	100	85	95	100	95	80	80	90	75	45	75	20	70	0	75	80	0	95
	31.25	70	90	80	90	100	80	70	40	80	0	0	70	0	0	0	0	30	0	95
244	500	100	100	45	100	100	100	90	100	100	40	40	90	20	40	40	95	80	0	90
	125	90	100	30	100	100	90	80	85	100	0	0	80	0	0	0	80	65	0	80
245	4000	0	—	—	—	—	—	50	0	30	—	—	—	—	0	0	0	—	0	0
246	500	80	70	85	100	90	80	50	100	70	0	70	95	0	50	75	90	75	0	80
247	500	0	70	70	70	20	20	0	70	40	0	0	0	0	0	0	0	0	0	0
248	500	50	100	40	75	0	0	0	0	100	0	50	80	0	0	0	0	0	0	0
250	500	0	70	50	30	50	50	25	40	70	0	0	0	0	0	0	0	0	0	0
255	2000	20	50	5	80	70	0	10	40	0	0	0	0	0	0	0	0	0	0	0
257	4000	0	—	—	—	—	—	20	100	60	—	—	—	—	0	0	0	—	0	0
258	4000	0	—	—	—	—	—	20	—	20	—	—	—	—	0	0	0	—	0	0
260	500	80	95	90	100	—	95	40	45	90	0	0	25	0	50	0	90	95	0	0
261	500	60	95	90	90	—	95	90	65	95	0	0	30	0	20	10	95	100	0	0
262	500	100	100	95	100	—	100	100	100	100	50	40	90	10	100	95	100	100	0	80
	31.25	80	100	90	100	—	100	90	100	95	0	0	75	0	80	65	95	100	0	15
263	500	50	100	0	100	—	80	80	90	40	0	85	70	0	40	90	95	100	0	0
264	250	0	50	70	80	—	80	80	50	0	0	0	20	0	20	0	60	10	0	0
265	500	0	60	40	80	—	0	60	70	0	0	0	0	0	0	0	0	0	0	0
266	500	10	75	80	30	—	90	85	25	75	0	40	0	0	75	70	80	0	0	0
267	500	0	80	45	80	—	80	90	60	95	0	40	65	0	35	90	70	75	0	40
268	31.25	100	100	10	—	95	80	90	100	100	0	10	75	0	100	0	85	0	0	95
269	62.5	80	90	0	100	0	80	90	30	100	0	0	50	0	30	0	0	70	0	0
270	62.5	70	80	10	100	60	—	55	100	70	35	0	50	0	60	70	70	0	40	50
	3.9	45	70	0	55	20	75	20	60	55	0	0	10	0	20	0	65	0	0	0

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POSTEMERGENT CONTROL OF PLANT SPECIES

Compound	Dosage (ppm)	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	T
		Plant Species																		
271	1000	65	80	40	100	50	—	60	100	80	0	0	50	0	85	80	90	30	0	50
	62.5	50	70	0	60	0	—	0	20	60	0	0	35	0	30	0	0	0	0	45
272	62.5	45	60	0	80	30	50	0	50	70	0	0	0	0	20	20	50	0	0	20
273	500	—	100	40	100	40	100	80	100	50	0	20	40	0	20	100	75	30	0	40
274	2000	80	90	46	100	75	80	80	100	100	50	70	100	0	100	98	98	80	0	80
275	125	—	—	0	—	80	98	60	100	—	60	0	—	0	20	100	90	80	30	60
276	125	—	—	0	—	70	100	65	100	—	80	0	—	40	90	90	80	90	0	70
277	125	0	—	50	—	60	80	20	100	—	75	80	—	20	25	70	80	—	0	25
	31.2	0	—	20	—	0	80	0	100	—	0	20	—	0	0	0	100	—	0	0
278	125	—	—	30	—	60	70	60	100	—	0	0	—	0	70	100	90	—	0	80
279	125	—	—	20	—	70	98	60	100	—	0	35	—	0	60	90	80	—	0	80
280	250	—	—	0	—	60	—	60	100	—	75	0	—	—	70	95	90	—	0	50
281	125	—	—	0	—	60	100	60	100	—	—	0	—	0	70	85	98	—	0	70
282	125	70	80	50	80	70	80	80	100	80	0	30	70	0	80	100	80	100	0	75
	31.2	60	80	20	—	50	70	50	100	85	0	0	50	0	80	70	75	98	0	20
283	125	50	80	80	80	70	100	80	100	80	0	50	80	0	80	90	80	90	0	25
284	125	—	—	0	—	70	100	80	100	—	20	0	—	0	75	80	85	90	30	70
285	125	80	90	70	90	70	100	50	100	98	0	60	50	0	80	80	85	100	0	60
	7.8	—	80	0	80	50	100	40	100	80	0	0	20	0	0	0	75	70	0	0
286	125	30	100	65	80	30	90	80	100	80	0	80	50	0	80	90	85	90	0	60
287	125	70	80	70	85	40	80	70	100	80	0	0	80	0	20	80	80	80	0	0
288	125	30	95	70	90	40	—	80	100	90	0	30	30	0	70	100	80	80	50	30
289	1000	50	98	55	90	70	100	80	100	80	0	35	80	0	80	90	85	80	0	0
290	125	30	80	50	85	40	100	80	100	80	0	50	50	0	80	100	70	80	50	25
291	125	40	85	40	85	60	100	30	100	80	0	20	50	0	80	95	80	85	0	20
	7.8	20	60	0	85	0	50	30	100	60	0	0	0	0	0	0	20	20	0	0
292	125	60	100	50	—	90	80	80	100	100	35	70	50	0	80	65	98	100	50	60
	31.2	40	95	0	—	60	70	80	100	95	0	60	40	0	20	20	98	75	—	20
293	125	90	100	30	100	90	80	0	100	98	0	60	80	0	70	80	100	80	50	0
	31.2	50	80	10	80	90	50	0	100	85	0	30	50	0	20	50	95	50	20	0
294	125	60	98	55	85	98	90	70	100	98	0	50	50	0	90	85	98	90	0	0
297	125	70	100	50	—	80	80	0	100	95	0	50	80	0	50	80	95	100	20	0
298	2000	35	95	30	80	90	80	50	100	85	0	50	60	20	70	65	98	60	40	20
	500	35	85	0	80	50	50	50	100	80	0	40	40	0	65	25	75	50	—	0
299	2000	0	50	0	80	0	0	40	100	50	0	0	0	0	0	0	0	50	0	0
300	125	60	98	15	85	70	85	60	100	85	0	30	20	0	70	75	85	70	0	0
	62.5	50	98	0	80	50	85	50	100	85	0	30	50	0	65	50	50	70	0	0
301	2000	30	90	15	85	60	—	50	100	90	0	0	25	0	30	70	100	50	0	0
304	62.5	90	95	80	—	95	95	85	100	90	0	40	20	0	50	55	90	—	0	60
305	250	90	98	98	98	98	90	70	100	100	0	90	95	0	25	15	90	97	0	40
306	125	50	—	98	90	—	—	80	100	90	0	60	60	0	30	80	98	50	0	70
307	250	70	95	40	35	90	—	90	100	50	70	90	30	0	75	25	—	50	80	35
308	1000	30	80	75	—	98	80	80	100	60	65	30	70	40	0	50	98	30	30	80
312	2000	0	70	40	30	0	25	—	0	40	0	0	0	30	0	0	0	0	0	0
313	1000	100	100	40	98	—	95	80	—	98	0	0	50	0	50	—	100	75	0	0
314	2000	40	80	15	80	—	80	80	—	80	0	60	0	0	20	80	98	80	0	0
315	1000	70	80	0	—	—	100	90	100	75	0	40	40	0	60	0	75	50	0	0
316	2000	80	100	0	80	—	100	80	—	85	0	30	25	0	0	50	80	80	0	0
317	31.3	75	80	80	90	75	90	80	90	95	90	90	30	30	60	80	75	80	75	80

-continued

POSTEMERGENT CONTROL OF PLANT SPECIES

Compound	Dosage (ppm)	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	T
		Plant Species																		
318	7.8	80	100	95	100	100	90	98	90	100	98	80	80	80	80	98	90	100	95	80
319	31.3	100	100	98	100	98	95	100	100	98	60	90	30	80	30	—	80	80	0	80
320	7.8	70	100	95	80	98	—	90	80	95	95	98	75	80	50	—	98	75	95	30
321	7.8	40	98	95	90	90	98	98	100	100	100	90	80	90	35	—	98	90	95	80
322	7.8	98	95	95	90	70	85	80	100	85	100	98	90	100	40	—	98	100	80	70
323	7.8	50	95	80	100	90	100	75	100	95	80	—	90	70	0	0	98	98	98	30
324	7.8	80	100	90	80	100	—	75	100	98	90	95	98	100	60	70	100	100	90	0
325	15.6	90	98	90	90	100	90	90	100	100	30	0	0	70	0	90	90	0	0	80
326	7.8	40	100	90	100	80	80	95	98	80	98	80	90	98	70	—	98	100	80	70
327	15.6	90	90	95	90	100	80	90	95	100	95	98	98	90	95	95	98	100	0	90
328	15.6	35	98	85	95	90	95	60	98	80	98	95	90	100	85	100	100	100	90	80
329	31.3	95	90	95	80	—	85	90	100	90	98	100	90	98	90	98	95	100	98	0
330	31.3	100	95	100	98	—	90	90	100	90	100	98	90	98	80	95	95	90	98	0
331	3.9	90	95	85	90	90	30	90	100	98	0	20	0	0	0	—	45	0	0	0
332	15.6	90	98	100	90	100	98	80	98	95	98	70	95	100	98	—	100	100	98	80
333	7.8	90	98	98	80	95	100	100	50	98	100	95	98	90	98	0	90	100	0	80
334	3.9	60	100	95	85	80	100	30	30	95	98	98	70	100	100	95	95	100	100	0
335	3.9	60	100	100	100	90	100	20	100	95	100	100	100	100	60	40	100	100	20	10
336	62.5	50	100	90	100	100	100	100	100	100	100	100	100	—	98	100	100	90	98	45
337	31.3	60	80	98	85	100	100	70	100	100	100	98	80	100	80	50	100	80	98	65
338	31.3	60	80	98	75	95	80	100	98	50	100	20	98	50	70	—	—	98	0	80
339	15.6	50	100	100	70	100	100	—	90	100	50	80	70	50	0	0	100	60	20	50
340	31.3	90	90	100	90	—	80	80	100	80	80	90	20	70	75	90	90	0	30	0
341	31.3	80	80	60	30	70	20	80	20	55	20	20	50	0	0	0	20	30	0	90
342	31.3	90	90	90	90	80	—	70	100	95	95	40	45	60	60	—	98	90	90	70
343	15.6	60	90	95	40	95	50	10	50	100	95	90	10	0	10	0	0	0	0	35
347	2000	55	100	60	80	0	0	0	30	40	98	25	50	—	0	—	0	90	30	0
348	125	0	70	45	50	0	0	0	40	30	0	0	0	0	0	0	15	0	0	0
350	125	0	90	0	60	0	0	0	100	100	0	90	20	0	0	0	100	60	0	0
351	2000	50	40	75	—	0	90	30	0	0	0	0	0	0	0	0	50	25	0	20
352	500	55	90	90	80	60	40	70	—	35	75	40	40	0	20	—	0	80	30	45

So as to clearly illustrate the phytotoxic properties of the various active ingredients of the present invention applied preemergently, a controlled greenhouse experiment is described below.

EXAMPLE 119

The seeds of various species of plants were planted in beds of good agricultural soil in a greenhouse. A number of compositions of the present invention, generally in the nature of an aqueous emulsion, were applied at rates listed in the table so as to deposit a predetermined amount of active ingredients uniformly throughout the surface of the bed. Another seed bed was treated only with water to serve as a control. After treatment the seed beds were maintained for two weeks under greenhouse conditions conducive for good plant growth and watered as necessary. The specific plant species, test compound, and dosage and the percent preemergent control at at least one dosage are set forth in the table below. Control refers to the reduction in growth compared to the observed results of the same untreated species.

PREEMERGENT CONTROL OF PLANT SPECIES

Compound	Dosage (lb/-acre)	Plant Species A	B	C	D	F	G	H	I	J	K	L	M	N	O	Q	R	P	T
1	10	—	—	—	—	—	90	100	90	—	—	—	—	70	100	—	70	100	—
2	0.5	0	95	30	70	0	100	30	95	15	20	60	0	80	95	50	30	95	0
4	10	98	—	—	—	—	90	100	90	—	—	—	—	100	80	—	90	100	—
6	0.5	100	100	95	95	0	30	70	60	10	90	50	50	90	70	10	—	50	40
	0.25	70	100	10	95	0	0	100	60	0	80	50	0	80	0	0	—	—	50
7	0.1	95	98	95	98	100	80	100	95	90	98	95	100	98	80	80	20	70	90
	0.125	20	98	20	90	0	40	50	40	0	70	70	0	30	0	10	0	20	0
8	1.0	100	100	95	100	100	60	100	90	95	100	—	55	95	95	95	70	95	95
	0.25	90	100	95	90	100	25	95	60	80	90	—	0	75	70	80	15	60	75
9	0.5	0	100	40	100	100	0	30	0	0	50	20	0	98	40	0	—	20	0
10	1.0	0	98	0	90	0	0	95	75	0	80	—	0	0	40	0	0	0	0
12	0.25	95	95	95	98	0	50	60	30	50	10	—	0	40	10	80	0	0	50
	0.125	80	95	40	95	0	0	0	20	0	0	—	0	10	0	50	0	0	30
13	0.25	95	98	95	98	70	90	95	95	80	95	98	20	95	80	95	10	90	98
	0.062	90	98	80	90	50	90	20	95	0	60	95	0	50	0	90	0	50	80
14	4.0	90	95	20	99	10	0	90	10	10	10	15	0	10	95	60	20	0	0
15	1.0	90	95	60	70	0	30	30	80	10	15	—	0	10	15	20	0	10	5
16	1.0	100	0	15	0	0	15	35	0	15	20	—	0	0	0	0	0	0	0
17	1.0	0	90	0	40	0	0	70	0	10	50	10	0	0	0	0	0	0	0
19	1.0	95	98	95	95	80	80	98	85	35	50	60	0	40	70	30	80	60	90
	0.25	90	95	20	90	0	50	90	70	0	20	0	0	0	20	0	0	0	40
21	2.0	80	95	70	98	70	60	100	75	50	80	—	0	0	60	40	0	0	60
22	0.25	95	100	95	98	100	70	100	98	50	90	95	50	95	95	98	90	98	98
	0.062	80	100	95	95	100	30	80	80	0	10	60	0	40	90	40	90	95	90
24	10	95	—	—	—	—	80	100	98	—	—	—	—	70	70	—	10	70	—
25	0.25	98	100	98	100	98	80	100	98	100	100	—	70	98	100	98	95	100	95
	0.062	95	98	95	95	70	40	0	70	98	95	—	0	60	20	90	0	50	50
26	0.25	95	98	98	100	100	95	100	95	100	100	—	0	98	100	98	40	100	100
	0.062	95	98	95	98	95	80	100	90	95	90	—	0	30	95	60	0	60	100
29	10	90	—	—	—	—	0	60	0	—	—	—	—	0	20	20	0	—	—
30	1.0	0	0	95	0	100	0	100	0	0	0	0	0	0	90	0	90	30	0
31	0.25	80	98	95	100	100	65	100	95	95	95	98	50	98	100	100	100	98	100
	0.062	70	60	90	90	100	0	95	90	0	10	50	0	98	95	90	0	98	80
32	0.5	50	100	90	100	100	98	95	100	20	60	40	40	100	98	100	100	98	50
	0.125	20	0	60	50	40	30	95	90	0	0	50	0	30	95	65	0	0	0
33	1.0	90	98	90	50	95	60	95	80	95	95	70	80	98	98	95	40	98	98
	0.25	20	80	10	50	40	0	0	10	0	0	0	0	70	50	10	0	40	0
34	1.0	95	100	95	95	95	80	98	95	60	70	80	0	70	20	95	30	40	90
	0.25	80	95	80	90	0	20	50	80	0	40	90	0	20	0	80	0	0	70
35	2.0	60	80	60	98	0	10	—	50	0	0	0	0	0	60	80	0	0	40
36	1.0	0	30	0	50	100	0	0	0	0	0	0	0	0	0	0	0	0	0
37	0.25	95	95	95	97	100	90	100	95	95	97	95	0	97	70	95	0	97	100
	0.062	95	93	35	100	40	30	100	90	20	50	30	0	30	0	50	0	20	97
39	0.25	95	95	95	97	100	90	100	95	95	97	95	0	97	70	95	0	97	100
	0.031	90	93	30	97	0	30	100	50	0	0	0	0	0	0	0	0	0	60
40	4	20	100	50	60	100	0	—	20	0	50	—	0	0	—	0	0	0	70
41	0.25	40	80	25	80	0	10	0	10	0	0	20	0	80	10	35	0	30	70
42	0.016	0	100	100	70	0	0	—	30	0	0	—	0	0	—	0	100	0	0
43	4.0	30	40	20	95	0	60	70	30	0	0	0	0	20	40	40	0	0	0
44	0.25	85	93	80	97	100	20	95	0	10	70	93	70	40	90	80	40	70	90
46	0.125	95	95	97	97	100	90	100	97	60	0	50	60	70	97	10	60	95	99
	0.031	95	95	93	97	100	70	100	80	0	0	0	0	0	70	0	0	30	97
47	2.0	97	97	97	100	97	70	99	99	0	0	0	30	—	40	20	30	—	97
	0.5	50	90	85	97	90	20	99	90	0	0	0	0	—	40	10	0	—	90
49	0.062	100	100	100	99	100	99	—	90	90	10	—	0	85	—	50	0	90	100
48	1.0	30	20	0	50	60	60	0	0	0	0	0	20	20	10	0	70	20	0
50	0.25	80	95	95	100	100	80	100	93	99	97	100	100	95	25	95	60	95	99
	0.062	0	93	85	97	75	40	80	90	90	100	80	0	97	0	90	10	93	99
51	0.25	93	95	90	95	95	80	100	95	97	80	97	97	97	95	95	100	97	100
	0.062	50	95	10	93	90	70	70	20	45	10	55	0	0	90	10	0	45	80
52	2.0	30	80	—	30	0	50	0	35	0	0	0	0	0	25	0	0	0	10
53	0.125	90	95	90	100	97	85	100	90	97	97	97	30	95	95	93	99	93	100
	0.031	20	93	20	100	85	40	95	0	20	80	15	0	10	80	75	0	60	97
54	0.125	95	93	95	97	99	70	100	90	95	99	97	0	93	95	95	40	95	97

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PREEMERGENT CONTROL OF PLANT SPECIES

Compound	Dosage (lb/-acre)	Plant Species A	B	C	D	F	G	H	I	J	K	L	M	N	O	Q	R	P	T
	0.031	85	93	35	97	90	0	100	20	0	93	50	0	15	10	40	0	45	55
56	0.25	0	100	0	100	0	90	—	50	30	0	—	0	0	—	0	0	20	70
57	4.0	100	100	100	100	0	0	—	0	40	0	—	0	20	—	80	0	50	0
58	0.062	0	100	0	100	100	80	—	100	70	0	—	0	30	—	80	50	90	100
59	20.0	0	100	60	100	90	35	—	50	0	0	—	0	0	—	0	0	0	0
60	0.5	0	50	20	0	0	100	—	0	50	0	—	0	0	—	0	40	0	0
61	5.0	100	100	100	100	100	100	—	70	85	100	—	0	65	—	90	0	100	90
62	0.5	0	90	50	50	0	0	—	20	0	80	—	0	20	—	0	0	20	60
63	0.125	100	100	100	100	100	0	—	100	30	90	—	40	10	—	0	0	30	100
64	0.062	50	100	100	90	100	70	—	90	60	0	30	0	0	—	40	0	90	90
65	0.25	0	20	100	100	90	50	—	20	0	30	—	0	70	—	95	0	95	95
66	10.0	100	—	—	—	—	100	100	100	—	—	—	—	80	100	—	50	100	—
67	10.0	30	—	—	—	—	100	30	30	—	—	—	—	70	—	—	40	—	—
68	1.0	100	100	80	90	100	0	—	90	80	0	90	20	70	—	50	20	80	50
69	0.5	100	100	50	100	0	30	—	40	93	0	100	70	0	—	20	0	70	100
70	1.0	90	100	70	95	100	30	—	80	100	40	90	80	40	—	90	60	90	95
71	10.0	98	—	—	—	—	50	100	70	—	—	—	—	50	98	—	70	100	—
72	0.25	40	100	90	90	100	10	—	60	90	70	80	90	30	—	50	90	50	100
73	0.125	0	30	0	0	0	0	0	0	0	0	40	0	0	0	0	0	0	0
74	0.125	90	100	100	100	100	0	—	70	0	0	100	0	30	—	70	0	70	100
75	0.5	0	100	0	90	0	20	—	90	0	0	0	—	20	—	0	0	80	0
76	0.25	60	100	95	100	100	90	—	100	100	70	90	100	70	—	80	90	90	100
77	0.25	0	80	80	50	90	60	—	0	70	40	50	0	20	—	0	0	80	90
78	0.25	0	100	30	70	0	0	—	30	10	40	0	40	20	—	0	30	20	50
79	0.5	40	100	40	70	90	10	—	30	50	30	10	0	0	—	0	—	0	0
80	10.0	0	—	—	—	—	—	100	80	—	—	—	—	0	0	—	—	0	—
82	0.125	0	90	0	90	0	0	0	0	0	0	0	0	0	0	0	0	0	0
83	0.5	0	98	0	30	50	0	—	20	0	0	0	0	0	0	0	0	0	0
84	10.0	30	—	—	—	—	20	90	98	—	—	—	—	0	0	—	0	0	—
85	0.125	90	100	100	100	100	90	—	100	70	0	0	0	20	—	30	0	60	100
	0.015	70	100	30	—	90	20	—	60	0	0	0	0	0	—	0	0	0	0
86	0.25	0	100	20	100	100	0	—	0	0	0	0	0	0	—	0	0	0	0
87	4.0	80	90	65	—	20	70	—	0	0	0	70	0	0	—	50	0	40	100
90	2.0	100	100	70	100	100	70	—	95	80	90	70	20	50	—	40	30	80	90
	1.0	90	100	50	100	60	30	—	30	70	20	40	0	0	—	30	0	80	100
91	0.25	100	100	100	100	100	40	—	100	60	30	50	0	20	—	40	0	70	100
	0.062	20	100	90	90	100	0	—	50	0	0	20	0	0	—	0	0	20	20
92	0.5	10	100	0	70	—	0	—	0	0	0	40	0	0	—	0	0	0	0
93	0.5	70	40	20	0	0	0	—	0	0	10	0	—	0	—	0	0	0	0
94	0.25	60	100	50	0	0	0	—	0	0	0	0	—	0	—	0	0	0	0
97	1.0	30	100	0	20	80	0	—	0	0	0	10	40	0	—	0	0	0	100
98	10.0	80	—	—	—	—	40	100	98	—	—	—	—	90	90	—	40	90	—
101	10.0	40	—	—	—	—	0	40	70	—	—	—	—	0	60	—	20	0	—
104	0.25	100	100	100	100	100	100	—	100	100	100	100	100	100	100	100	100	100	100
	0.016	100	100	80	100	80	100	—	100	95	95	100	100	100	—	100	90	95	100
106	1.0	95	95	95	100	100	85	—	98	98	70	98	98	70	20	95	98	70	80
108	0.5	95	95	100	80	80	70	80	98	95	100	70	98	85	95	98	50	50	90
	0.125	40	95	30	70	70	50	40	90	60	80	10	30	0	0	50	0	0	60
110	2.0	0	50	0	0	0	0	—	0	90	40	50	0	80	0	0	0	0	0
111	0.25	20	95	10	90	95	20	50	80	35	65	65	0	15	90	75	0	30	93
112	0.25	80	85	0	99	0	80	90	20	50	25	20	0	0	97	30	90	0	90
113	0.25	30	90	0	100	0	0	100	60	0	40	0	0	20	90	50	0	50	50
114	0.5	95	95	15	50	100	50	100	60	0	80	40	0	0	0	10	0	10	80
116	0.5	90	100	10	100	100	20	—	60	0	0	0	—	0	—	0	0	0	30
117	0.5	90	100	20	90	90	20	—	90	0	0	0	0	0	—	60	0	40	0
118	0.5	30	90	0	60	0	0	—	0	0	0	0	—	0	—	0	0	0	0
119	0.5	90	100	0	90	100	0	—	20	0	0	50	0	0	—	0	0	0	70
120	0.25	70	90	0	80	95	100	—	10	20	0	0	75	0	50	30	0	80	—
128	1.0	20	100	0	90	100	0	—	30	0	0	50	0	0	—	0	0	0	0
136	1.0	30	65	0	0	0	0	—	98	0	0	0	—	0	0	80	—	0	10
137	0.25	80	—	0	100	10	70	—	80	0	50	30	30	20	—	20	—	20	100
138	0.25	100	100	50	90	20	20	—	90	30	50	50	10	0	—	90	—	90	80
139	0.25	100	100	50	100	100	90	—	100	70	90	100	80	80	—	100	—	100	100
140	0.125	100	100	50	100	60	80	—	90	0	—	70	10	70	—	70	0	80	100
141	0.25	100	100	100	100	100	100	—	100	100	100	100	95	95	—	100	—	100	75
142	0.5	20	20	0	100	100	0	100	40	0	0	50	0	0	0	0	0	0	25
143	0.25	100	95	70	100	100	90	100	97	95	97	99	50	97	100	100	50	97	100
	0.062	95	95	25	100	100	80	100	95	60	80	99	0	97	50	85	0	95	100
	0.016	95	95	25	100	40	0	40	90	0	70	20	0	75	0	75	0	50	75
144	0.25	100	100	60	100	100	95	—	100	70	40	—	0	80	—	100	70	100	100
	0.062	100	90	70	100	100	0	—	60	0	0	—	0	60	—	60	0	93	80
145	0.125	100	100	40	100	100	60	—	100	0	0	—	0	0	—	50	0	20	80
	0.062	90	90	0	100	50	100	—	90	0	0	—	0	0	—	20	0	0	40
146	0.125	100	85	0	100	—	90	—	90	60	60	—	0	100	—	97	0	95	100
	0.062	60	30	0	90	—	0	—	20	0	30	—	0	95	—	90	0	85	100
147	0.031	70	100	0	100	100	20	—	20	20	0	30	0	—	0	90	0	100	
148	0.125	30	90	0	100	100	0	—	50	20	0	—	0	30	—	90	0	70	100

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PREEMERGENT CONTROL OF PLANT SPECIES

Compound	Dosage (lb/acre)	Plant Species A	B	C	D	F	G	H	I	J	K	L	M	N	O	Q	R	P	T
149	10	30	—	—	—	—	40	40	50	—	—	—	—	50	50	—	20	20	—
150	0.5	90	100	30	90	100	80	—	20	80	0	95	50	30	—	70	50	80	95
151	0.031	100	100	0	100	100	30	—	90	30	30	40	50	60	—	50	30	60	100
152	0.031	90	100	0	100	100	60	—	100	0	0	40	0	40	—	30	0	90	100
153	0.031	100	100	0	100	100	20	—	100	30	20	20	0	65	—	30	0	70	100
154	0.125	30	100	0	90	100	0	—	20	0	0	10	0	0	—	0	0	0	100
156	0.125	90	100	0	100	100	70	—	90	0	50	90	0	60	—	20	30	20	95
157	0.031	100	100	0	100	90	50	—	100	0	20	50	0	10	—	90	0	80	30
158	0.031	90	100	0	100	80	20	—	100	0	20	30	0	40	—	0	0	30	0
159	0.062	100	100	0	100	100	60	—	100	50	90	70	0	80	—	80	0	75	70
160	0.62	100	100	0	100	100	80	—	100	35	0	60	0	0	—	0	0	30	100
	0.015	90	100	0	100	100	80	—	80	0	0	0	0	0	—	0	0	0	100
161	10	100	—	—	—	—	100	100	100	—	—	—	—	100	100	—	100	100	—
162	0.125	80	100	10	100	0	0	—	90	0	0	50	0	40	—	30	30	80	100
163	2	100	100	0	100	100	0	—	60	40	0	0	0	0	—	0	0	0	60
164	0.125	90	100	10	100	100	20	—	100	0	0	20	0	0	—	0	0	60	90
	0.031	70	100	0	90	70	0	—	100	0	0	0	0	0	—	0	0	20	90
165	0.25	90	75	10	90	90	60	—	30	0	0	60	0	60	—	0	0	90	90
166	0.25	100	100	80	100	90	95	—	100	10	40	80	20	80	—	20	30	80	100
	0.062	80	90	40	100	70	0	—	90	0	0	0	0	70	—	0	0	50	100
169	10	90	—	—	—	—	100	100	98	—	—	—	—	50	40	—	—	50	—
170	0.25	70	100	0	90	0	30	—	85	20	30	80	10	40	—	90	—	70	0
171	0.25	70	100	20	100	20	50	—	90	40	90	100	50	100	—	100	—	100	80
172	0.25	100	—	90	100	100	90	—	100	80	100	100	90	100	—	90	—	100	100
	0.31	80	—	0	100	40	80	—	90	20	0	90	60	0	—	70	0	0	100
173	0.25	50	80	0	90	0	0	—	0	30	70	30	20	30	—	70	—	50	0
175	0.125	100	100	100	100	100	100	—	100	100	100	100	100	100	—	100	—	100	100
	0.016	70	100	0	100	60	0	—	60	0	0	30	0	50	—	50	0	80	70
178	0.25	65	80	0	95	0	10	60	40	0	0	0	—	25	0	0	—	0	0
181	0.25	98	100	80	98	98	80	—	98	0	30	95	0	20	—	60	40	80	50
182	0.12	98	98	98	98	99	98	—	98	0	0	20	0	0	—	70	0	90	100
183	0.5	98	98	0	100	98	0	—	100	0	0	90	0	0	—	0	0	0	0
184	0.25	100	98	50	100	98	80	—	100	0	0	95	0	0	—	30	0	80	80
185	0.25	98	100	70	98	90	80	—	100	0	20	90	0	20	—	90	0	—	0
186	0.062	90	98	20	90	90	0	—	95	0	0	30	0	30	—	40	0	50	30
187	10	100	—	—	—	—	100	100	100	—	—	—	—	100	100	—	100	100	—
188	10	98	—	—	—	—	100	100	100	—	—	—	—	100	100	—	100	100	—
189	0.25	100	100	80	100	80	50	—	100	80	90	100	80	80	—	70	—	80	100
	0.063	80	100	60	80	0	50	0	70	0	10	10	50	70	—	50	—	40	100
190	0.25	90	—	90	100	90	50	—	50	10	20	95	20	30	—	30	—	70	100
191	0.25	100	100	100	100	100	100	—	100	95	—	100	100	100	—	100	—	100	100
192	0.25	95	100	90	100	100	97	—	100	10	0	—	0	0	—	0	0	70	90
193	0.125	90	100	0	100	100	40	—	60	0	0	0	0	0	—	20	0	0	0
194	0.25	90	100	70	100	95	90	—	90	0	0	30	0	0	—	0	0	0	95
195	0.125	30	100	0	95	100	60	—	70	10	0	0	0	0	—	0	0	20	100
196	0.125	95	100	0	95	100	60	—	70	0	0	0	0	0	—	0	0	0	20
197	0.125	99	99	30	99	99	80	—	99	0	40	20	10	50	—	80	10	98	90
198	4	90	100	0	100	0	0	—	80	10	70	20	50	0	—	70	70	0	30
199	0.25	20	100	70	90	0	20	—	70	0	0	—	—	—	—	0	0	0	0
200	0.5	100	100	100	100	100	60	—	90	50	0	10	0	0	—	0	0	0	60
202	4	0	20	40	100	0	100	—	0	0	0	—	0	0	—	0	0	0	0
203	1.0	40	100	0	80	0	0	—	0	0	0	0	0	0	—	0	0	0	0
204	0.25	80	40	0	90	—	0	—	0	40	0	60	0	0	—	0	0	0	0
205	0.25	100	100	90	100	100	75	—	100	95	50	—	0	50	—	0	50	0	70
206	0.5	100	100	100	100	50	35	—	100	0	0	—	0	40	—	40	0	60	97
208	0.25	100	100	45	100	90	40	—	90	0	0	30	0	0	—	0	0	0	60
209	10	100	—	—	—	—	100	100	90	—	—	—	—	70	100	—	70	50	—
211	10	90	—	—	—	—	80	80	95	—	—	—	—	—	80	—	50	90	—
212	1	30	30	70	90	30	0	—	40	10	0	0	0	0	—	0	0	0	0
213	0.125	100	—	70	100	90	80	—	100	100	10	100	70	80	—	180	50	100	—
	0.031	50	—	0	60	90	50	—	100	10	0	50	0	0	—	50	0	0	—
214	0.25	100	100	100	100	100	100	—	100	100	100	100	100	100	—	100	100	100	100
	0.031	100	100	50	100	100	70	—	100	90	80	100	100	70	—	90	100	100	70
215	0.25	100	100	100	100	100	100	—	100	100	100	100	100	100	—	100	100	100	100
	0.031	70	100	70	100	100	100	—	100	70	60	100	50	10	—	90	50	90	95
216	0.25	100	20	70	100	100	90	—	100	100	90	100	100	75	—	100	100	100	70
	0.063	50	0	10	70	100	50	—	70	50	50	50	100	70	—	70	90	100	70
217	0.25	100	100	100	100	100	100	—	100	50	90	100	100	90	—	100	—	50	70
	0.125	100	100	100	100	100	100	—	100	0	0	100	50	30	—	90	—	30	70
218	0.25	100	100	100	100	100	100	—	100	0	0	95	0	0	—	50	—	50	50
219	0.25	100	100	100	100	100	100	—	100	100	50	100	100	100	—	100	—	100	100
	0.031	100	100	30	100	100	100	—	100	70	10	70	100	0	—	100	—	70	70
220	0.25	100	100	90	100	100	70	—	100	100	50	100	100	90	—	100	—	100	100
	0.063	50	80	0	100	90	30	—	100	50	50	10	100	90	—	90	—	100	50
221	0.25	100	100	100	100	100	100	—	100	90	100	100	90	100	—	70	—	100	100
	0.031	70	60	0	70	75	90	—	100	0	0	30	0	90	—	0	—	50	70
222	0.25	100	100	100	100	100	90	—	100	40	90	50	0	0	—	100	—	30	50

-continued

PREEMERGENT CONTROL OF PLANT SPECIES

Compound	Dosage (lb/acre)	Plant Species A	B	C	D	F	G	H	I	J	K	L	M	N	O	Q	R	P	T
	0.125	100	100	60	100	100	90	—	100	0	100	30	0	0	—	70	—	30	50
223	0.25	100	100	100	100	100	100	—	100	100	95	100	100	100	—	100	80	100	100
	0.031	95	100	100	100	100	100	—	100	90	100	100	90	100	—	100	80	75	75
227	0.25	60	100	0	100	100	70	—	30	40	50	100	90	50	—	70	—	90	100
228	0.25	90	80	20	100	100	70	—	90	50	—	100	50	90	—	90	—	50	50
229	0.25	100	100	30	100	90	100	—	90	40	10	90	0	0	—	0	—	0	100
230	0.25	100	90	20	100	100	90	—	90	90	50	100	30	100	—	90	—	80	100
	0.063	80	30	0	100	100	30	—	90	40	50	70	30	0	—	70	—	30	50
231	0.063	100	100	20	100	100	100	—	75	100	—	100	80	95	—	100	50	95	90
232	10	90	—	—	—	—	80	98	98	—	—	—	—	40	90	—	-40	98	—
233	1	80	100	20	80	90	70	—	70	0	0	0	0	0	—	0	0	0	0
234	2	80	100	0	0	40	0	—	0	10	0	30	0	0	—	30	0	0	100
235	0.25	50	—	0	50	50	90	—	20	50	10	50	50	—	—	0	—	20	0
236	10	100	—	—	—	—	100	100	100	—	—	—	—	100	100	—	100	100	—
237	0.25	50	—	40	50	10	20	—	0	20	20	20	100	10	—	10	—	30	30
238	10	0	—	—	—	—	0	80	60	—	—	—	—	0	0	—	0	0	—
239	10	90	—	—	—	—	100	100	100	—	—	—	—	95	98	—	98	98	—
243	0.125	90	100	100	100	100	80	—	60	75	0	90	0	70	—	80	0	80	100
244	0.125	70	100	20	100	100	0	—	100	0	0	0	0	0	—	0	0	0	95
245	10	0	—	—	—	—	100	0	60	—	—	—	—	0	0	—	0	0	—
246	0.25	80	80	90	90	0	0	—	30	20	20	95	10	0	—	20	40	20	20
247	2.0	80	100	100	100	100	0	—	80	85	70	80	70	60	—	90	90	70	30
250	0.5	0	100	0	30	0	10	—	0	0	0	50	40	10	—	30	100	0	0
252	10	0	100	100	100	100	50	—	0	80	100	—	30	60	—	50	50	80	90
255	4.0	60	90	15	80	40	0	95	0	0	10	30	0	0	0	40	60	0	15
257	10	90	—	—	—	—	80	100	90	—	—	—	—	0	30	—	0	30	0
258	2.0	0	10	20	0	100	0	90	20	0	30	0	0	0	60	0	0	0	0
260	1.0	20	80	0	80	90	50	—	70	0	0	—	0	0	—	40	0	30	70
261	2.0	0	100	100	90	—	90	—	80	0	0	—	0	0	—	10	70	50	0
262	0.25	90	100	100	100	100	90	—	100	80	95	—	0	90	—	60	50	95	100
263	0.5	0	40	0	100	0	50	—	20	0	0	—	0	0	—	0	50	50	0
264	2.0	0	60	0	40	100	0	—	0	10	0	—	0	0	—	0	0	0	0
265	10	0	—	—	—	—	60	60	30	—	—	—	—	0	0	—	0	0	—
266	4.0	50	100	50	90	80	0	—	0	0	0	30	40	0	—	0	50	90	80
267	4.0	0	100	30	80	90	0	—	90	70	30	30	50	20	—	10	50	90	0
268	0.25	100	100	0	100	100	90	—	100	80	100	100	—	90	—	80	30	100	100
	0.015	70	100	0	90	90	0	—	20	0	0	60	0	40	—	40	0	60	97
269	0.062	100	100	0	90	90	0	—	90	0	0	70	0	20	—	10	0	70	90
270	2.0	100	100	0	100	100	95	—	98	90	100	98	70	98	—	98	80	100	100
	0.125	98	98	0	98	100	90	—	98	30	70	90	0	95	—	90	20	95	100
272	0.5	90	100	0	100	100	60	—	100	50	40	50	0	75	—	60	0	95	100
	0.25	80	100	0	100	90	40	—	100	0	30	40	0	60	—	40	0	90	100
273	10	98	—	—	—	—	98	100	98	—	—	—	—	95	98	—	90	100	—
274	2	100	100	20	100	100	90	—	100	80	95	100	30	90	—	80	20	100	100
	0.25	95	100	0	100	90	80	—	100	60	80	90	0	80	—	70	0	95	100
275	0.25	100	100	20	100	100	90	—	100	80	90	100	100	100	—	100	—	100	100
	0.063	80	100	0	95	50	50	—	100	30	0	60	20	50	—	90	—	90	0
276	0.25	80	100	10	100	100	90	—	100	60	90	100	80	100	—	90	—	100	100
	0.063	70	100	0	100	100	80	—	100	0	10	90	50	70	—	80	—	90	100
277	0.25	50	100	20	100	100	30	—	100	40	80	90	80	90	—	100	—	100	100
278	0.25	100	100	70	100	100	100	—	100	60	90	100	70	100	—	90	—	100	100
	0.063	100	100	0	100	60	100	—	100	0	50	70	30	50	—	90	—	80	100
279	0.25	90	100	20	100	100	90	—	100	80	100	100	90	100	—	100	—	100	100
	0.063	100	100	0	100	100	90	—	100	0	40	90	60	50	—	80	—	100	100
280	0.25	80	100	10	100	100	90	—	100	50	50	100	60	100	—	90	—	100	100
	0.063	80	100	0	100	100	70	—	100	10	50	50	90	50	—	80	—	100	100
282	0.25	100	100	50	100	100	80	—	100	95	100	100	70	70	—	100	100	100	100
	0.063	100	100	10	100	70	80	—	100	0	50	90	50	70	—	100	100	80	70
283	0.25	100	100	20	100	95	80	—	100	40	100	100	100	100	—	100	—	100	100
	0.063	100	100	0	100	70	70	—	100	0	80	90	50	85	—	90	—	70	90
284	0.25	100	100	20	100	100	80	—	100	85	100	100	100	100	—	100	90	100	100
	0.063	70	100	0	100	85	70	—	100	0	70	90	50	100	—	70	10	70	100
286	0.25	100	100	30	100	100	100	—	100	50	100	100	70	100	—	100	—	100	100
	0.063	100	100	0	100	100	100	—	100	0	95	30	0	95	—	80	—	100	85
287	0.25	100	100	30	100	100	100	—	100	60	100	100	70	100	—	100	—	100	100
	0.063	100	100	0	100	100	50	—	100	0	80	70	100	100	—	80	—	100	70
288	0.25	100	100	40	100	100	100	—	100	80	100	100	60	100	—	100	90	100	100
	0.063	100	100	0	100	50	100	—	100	0	100	95	0	75	—	100	80	100	60
289	0.25	100	100	50	100	100	100	—	100	95	—	100	80	100	—	100	100	100	100
	0.063	100	100	0	100	80	70	—	100	60	—	95	50	60	—	95	50	100	50
290	0.25	100	100	70	100	100	100	—	100	90	100	100	95	100	—	100	70	100	80
	0.063	100	100	20	100	100	40	—	100	60	50	100	20	70	—	100	20	90	50
291	0.25	100	100	20	100	100	90	—	100	55	100	100	100	100	—	100	70	100	100
	0.063	100	100	0	100	100	0	—	100	0	70	100	30	75	—	100	70	90	100
293	0.25	100	100	10	100	100	70	—	100	60	90	100	60	100	—	95	95	100	100
	0.063	100	75	0	100	95	20	—	80	0	100	60	0	20	—	50	50	65	0
297	0.025	100	100	50	100	100	95	—	100	80	100	100	60	100	—	100	80	100	100

-continued

PREEMERGENT CONTROL OF PLANT SPECIES

Com-pound	Dosage (lb/-acre)	A	B	C	D	F	G	H	I	J	K	L	M	N	O	Q	R	P	T
		Plant Species																	
	0.063	100	100	0	100	90	85	—	100	0	50	90	20	65	—	70	50	40	90
298	0.25	100	100	0	100	100	70	—	100	40	95	95	50	100	—	95	50	100	100
	0.063	90	100	0	85	0	0	—	70	0	50	60	20	50	—	75	20	20	40
304	0.125	100	97	90	100	95	40	100	95	90	95	97	0	55	20	95	0	93	97
	0.031	70	95	40	100	20	0	100	60	0	10	10	0	0	0	10	0	20	35
305	1.0	97	97	95	100	80	90	100	95	90	98	100	0	93	50	95	0	50	100
306	0.125	90	100	70	90	100	40	—	100	0	0	40	0	0	—	80	0	20	70
307	0.250	70	100	60	85	55	100	—	0	0	10	30	100	0	60	100	10	60	—
313	0.250	90	0	0	0	0	—	—	0	0	0	0	0	0	0	50	0	0	—
314	0.250	50	90	0	0	0	0	—	0	60	0	0	0	0	0	0	0	0	—
317	0.250	95	100	95	95	95	80	95	85	100	100	100	100	80	70	95	95	90	100
318	0.125	100	100	90	100	90	98	90	90	100	90	95	98	70	90	95	70	90	100
319	0.125	80	100	90	90	95	80	100	100	80	0	0	0	0	20	100	0	50	90
320	0.063	100	100	80	100	90	50	60	90	90	100	100	100	100	90	90	50	100	95
321	0.125	90	100	50	80	90	80	100	80	95	100	90	90	90	90	90	75	90	100
322	0.125	80	80	20	80	90	60	55	30	90	90	90	90	50	85	80	60	90	100
323	0.125	90	90	90	90	90	90	75	80	80	100	100	100	100	80	90	40	90	100
324	0.063	50	90	90	100	85	60	90	20	90	95	40	50	50	0	85	50	90	20
325	0.125	90	90	90	90	95	95	80	80	90	0	40	0	0	0	0	0	0	100
326	10	—	—	—	—	—	80	100	80	—	—	—	—	100	100	—	100	100	—
327	10	—	—	—	—	—	90	100	90	—	—	—	—	100	100	—	100	100	—
328	0.063	75	100	95	100	90	90	75	85	70	95	90	95	100	90	100	80	100	70
329	0.063	90	90	95	95	90	75	80	0	90	98	100	95	90	90	100	90	90	100
330	0.063	90	100	80	100	0	100	90	70	90	50	15	60	75	60	90	20	70	100
331	0.063	60	100	90	95	90	50	100	60	90	25	0	20	0	0	0	0	50	95
332	0.063	90	0	100	90	90	100	100	75	85	90	70	95	100	100	90	60	90	90
333	10	—	—	—	—	—	100	100	100	—	—	—	—	100	100	—	100	100	—
334	0.063	90	100	90	100	90	80	100	0	100	100	90	95	100	90	90	60	90	0
335	0.063	100	100	90	90	80	70	60	20	50	100	30	75	80	80	70	70	60	90
336	0.063	75	95	95	98	90	50	90	80	90	95	100	70	95	60	100	40	90	100
337	0.063	0	90	40	0	75	100	90	30	50	80	0	0	0	50	0	0	75	85
338	0.063	0	0	60	70	70	100	75	50	20	75	40	75	30	60	0	0	0	100
339	0.125	80	100	50	90	80	—	70	20	90	35	0	25	0	25	—	0	55	100
341	10	—	—	—	—	—	70	100	80	—	—	—	—	95	100	—	50	80	—
342	0.125	0	—	0	25	50	0	90	0	50	0	0	0	0	0	60	0	90	95
343	0.125	0	70	15	0	35	0	0	0	0	0	30	20	0	45	50	0	70	95

Certain of the compounds of this invention have been found to be useful for the control of aquatic weeds and some of these are useful for the selective control of, e.g., barnyardgrass and yellow nutsedge in paddy fields in the presence of rice. The following example illustrate the utility of the compounds of this invention in aquatic weed control.

EXAMPLE 120

In testing for such utility, the plant species to be tested were transplanted into 16 oz. containers into about 2 inches of soil when they were in the 1-2 inch stage and then flooded to a depth of about 1 inch. An acetone concentrate of the chemical to be tested was then injected into the paddy water, the volume injected being varied as desired to provide the desired concentration. Percent control was evaluated nine days after application. The results were as follows:

CONTROL OF AQUATIC PLANT SPECIES

Compound	Dosage (Kg/Ha)	K	N	S	T
		Plant Species			
1	2.0	97	95	90	70
2	2.0	97	97	99	93
4	2.0	90	95	45	80
6	1.0	93	99	20	90
7	1.0	97	99	93	90
8	1.0	97	99	0	93
9	1.0	25	99	97	85
	0.25	0	93	80	30
10	1.0	93	90	50	90
12	1.0	70	97	0	95
13	0.25	97	93	10	93

-continued

CONTROL OF AQUATIC PLANT SPECIES

Compound	Dosage (Kg/Ha)	K	N	S	T
		Plant Species			
15	4.0	35	25	0	70
17	4.0	97	40	0	90
22	0.25	97	97	30	97
25	0.25	97	95	0	90
26	0.125	93	90	0	95
31	0.125	90	97	45	97
32	0.5	93	97	95	95
33	1.0	97	97	90	97
38	0.25	97	99	85	97
	0.031	0	80	0	95
39	0.25	75	99	75	99
	0.031	0	20	0	85
41	1.0	97	99	95	80
49	0.5	97	97	97	99
	0.016	0	50	0	95
50	0.125	97	97	97	97
51	1.0	95	97	70	97
	0.031	0	35	0	93
53	0.5	99	99	97	99
	0.031	0	80	10	95
54	0.5	97	97	0	95
108	1.0	97	97	97	90
111	4.0	93	99	80	99
114	1.0	70	95	0	90
	0.25	0	80	0	65
143	0.5	95	99	97	97
	0.031	0	95	0	93
178	2.0	50	20	0	90
180	1.0	80	97	97	97
	0.25	0	90	0	90

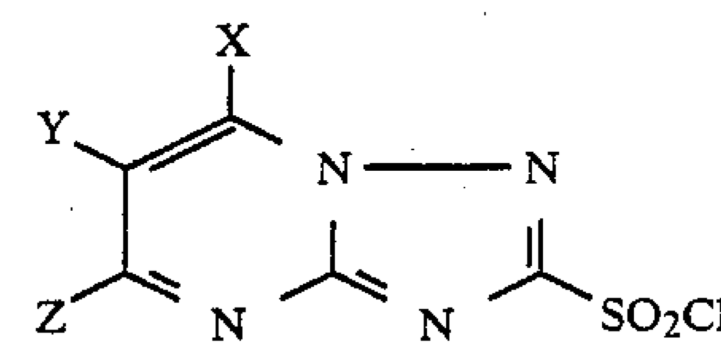
EXAMPLE 121

A post-emergence test comparing the herbicidal activity of Compound 157 (acid) with various of its amine salts was conducted using the protocol of Example 118 except that aqueous solutions of the amine salts and wettable powder formulation of Compound 157 were employed and only lambsquarters, morning glory, and soybeans were tested. In each case, 0.25 percent v/v of X-27 non-ionic surfactant was added. The following results were obtained at the application rates given:

Compound	Application rates g/Ha	Percent Control lambsquarters	morning glory	soybean
acid	280	100	50	20
	70	90	20	10
ethanolamine	280	100	80	60
salt	70	100	50	25
ammonium salt	280	100	70	60
	70	80	50	40
triethanolamine	280	100	80	65
salt	70	100	60	40
dimethylamine	280	100	50	50
salt	70	100	60	20
piperidine salt	280	100	80	45
	70	70	50	15

We claim:

1. A compound having the formula



wherein

X represents H, OCH_3, OC_2H_5, or CF_3, Y represents H, and Z represents CH_3 or OCH_3; wherein X represents Cl, Y represents H, and Z represents CH_3 or Cl; or wherein X and Z each represent H and Y represents Cl.

2. A compound of claim **1** which is 5-methyl-1,2,4-triazolo[1,5-a]pyrimidine-2-sulfonyl chloride.

3. A compound of claim **1** which is 5-methyl-7-methoxy-1,2,4-triazolo[1,5-a]pyrimidine-2-sulfonyl chloride.

4. A compound of claim **1** which is 5-methyl-7-ethoxy-1,2,4-triazolo[1,5-a]pyrimidine-2-sulfonyl chloride.

5. A compound of claim **1** which is 5-methyl-7-trifluoromethyl-1,2,4-triazolo[1,5-a]pyrimidine-2-sulfonyl chloride.

6. A compound of claim **1** which is 6-chloro-1,2,4-triazolo[1,5-a]pyrimidine-2-sulfonyl chloride.

7. A compound of claim **1** which is 5,7-di-methoxy-1,2,4-triazolo[1,5-a]pyrimidine-2-sulfonyl chloride.

* * * * *

UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 4,886,883

DATED : December 12, 1989

INVENTOR(S) : William A. Kleschick, Robert J. Ehr, Mark J. Costales, Ben C. Gerwick, Richard W. Meikle, William T. Monte, Norman R. Pearson

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

On the title page, under "Related U.S. Application Data", after the second listing of "Ser. No.", delete "768,353" and insert -- 768,393 --;

On the title page, under "OTHER PUBLICATIONS", after "Davey;", delete "E." and insert -- D. --;

Col. 2, line 14, delete "thone" and insert -- th one --;

Col. 4, line 56, delete "OCF_2CF_2H" and insert -- $-OCF_2CF_2H$ --;

Col. 4, line 67, delete "$-SOCF_2$ CF_2H," and insert -- $-SOCF_2CF_2H$, --;

Col. 5, line 5, delete "$C_3 14\ C_4$" and insert -- C_3-C_4 --;

Col. 5, line 21, after "Br" insert a comma;

Col. 10, line 65, before "NaOH)", insert -- a compound of Formula V using an appropriate base (i.e., --;

Col. 16, line 67, after "rides" insert a comma;

Col. 19, under "<u>SCHEME XIII</u>", delete "COOH" and insert -- COOR --;

Col. 23, line 40, delete the fifth and sixth letters "C" and "E" under the column "Compound" and insert -- G -- and -- H --;

Col. 33, line 11, "perchlorate" has been misspelled;

Col. 36, line 6, delete "broad t), 3.18 (2H, broad t) and 2.2-2.8 (5H,";

Col. 5, line 22, "alkyll" should read --alkyl--;

UNITED STATES PATENT AND TRADEMARK OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 4,886,883

DATED : December 12, 1989

INVENTOR(S) : William A. Kleschick, Robert J. Ehr, Mark J. Costales, Ben C. Gerwick, Richard W. Meikle, William T. Monte, Norman R. Pearson

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

Col. 36, line 25, "sulfonyl" has been misspelled;

Col. 38, line 51, delete "$C_8H_9ClN^4O_2S$:" and insert -- $C_8H_9ClN_4O_2S$: --;

Col. 39, line 62, delete "produce" and insert -- product --;

Col. 49, line 28, delete "5 ml" and insert -- 50 ml --;

Col. 57, line 1, delete "with diethyl ether (2X100 ml) and the aqueous phase";

Col. 114, line 5, delete "sulfuric" and insert -- sulfonic --.

Signed and Sealed this

Seventeenth Day of March, 1992

Attest:

HARRY F. MANBECK, JR.

Attesting Officer

Commissioner of Patents and Trademarks